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(54) Title: PHOTSENSITIVE ADHESIVE COMPOSITION

(54) Titre : COMPOSITION ADHESIVE PHOTSENSIBLE

(57) Abstract: The invention relates to a photosensitive adhesive composition of the polymerisable resin type, the hardening of which occurs by means of polymerisation and/or reticulation, characterised in comprising: - initiating means for at least one chain polymerisation reaction to guarantee the hardening of said composition and a sufficient quantity of at least one bifunctional monomer, comprising a photolabile centre with at least one photolabile entity and at least two polymerisable units, connected by covalent skeletons to said photolabile centre and located away from the cleavage sites of said photolabile centre, such that said composition loses the integrity and adhesivity thereof under the influence of a reticulating radiation causing the cleavage of the photolabile sites. The composition is particularly of application in dentistry.

(57) Abrégé : L'invention concerne une composition adhésive photosensible du type résine polymérisable dont le durcissement est obtenu par polymérisation et/ou réticulation, remarquable en ce qu'elle contient : - des moyens d'amorçage d'au moins une réaction de polymérisation en chaîne, afin d'assurer le durcissement de ladite composition, et - une quantité suffisante d'au moins un monomère bifonctionnel incluant d'une part, un noyau photoclivable comportant au moins une unité photoclivable et d'autre part, au moins deux unités polymérisables liées par des squelettes covalents audit noyau photoclivable et situées de part et d'autre du ou des sites de clivage dudit noyau photoclivable, afin que ladite composition durcie perde son intégrité et son adhésivité sous l'action d'un rayonnement de déréticulation procurant le clivage des unités photoclivables. Cette composition trouvera notamment une application dans le domaine dentaire.

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PHOTOSENSITIVE ADHESIVE COMPOSITION

The present invention pertains to a photosensitive adhesive composition. It also concerns a method for preparing certain bifunctional monomers that are constituents of this composition, and some of these special monomers.

5 In the area of dentistry the use of adhesives is well known, such as acrylic resins, used to ensure the fixing of elements onto teeth. For example, for positioning an orthodontic brace, attachments are fixed to the enamel surface of the teeth called brackets which are intended to hold the retaining wire in
10 place. Once correction is completed, these attachments are removed. Removal is generally achieved by traction/twisting using a gripping device. This is often a long and traumatizing operation for young patients and may cause substantial deterioration of the enamel surface that is sometimes
15 irreversible.

Similarly, mechanical deterioration of the supporting tissue is encountered when removing a crown, facet, post or inlay.

An adhesive has therefore been sought which enables two
20 parts bonded by this same adhesive to be separated without any mechanical damage to the surface of said parts. This adhesive would therefore have the particularity of losing its adhesiveness other than through external mechanical action. Preferably, this loss of adhesiveness should be obtained without having recourse
25 to solvents, but rather to un-crosslinking actinic radiation of said adhesive which would be the most suitable for dental applications.

In this respect, patent US 4 286 047 is also already known published on 25 August 1981 which discloses a pressure-sensitive
30 adhesive whose adhesiveness can be "released on demand" by exposure to UV radiation. The composition of this adhesive firstly comprises acrylate compounds polymerizable per se, which imparts the pressure-sensitive characteristic to the adhesive, and secondly cationic photoinitiators and monomer compounds
35 incorporating oxirane cycles. The photo-initiators are able to

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initiate the polymerization of the oxirane cycles after UV radiation. This photoinduced polymerization deteriorates the adhesive structure and greatly reduces adhesion to the substrate on which the adhesive composition was applied. This adhesive is
5 preferably used in adhesive tape or film form which is the most appropriate method of application for pressure-sensitive adhesives.

However, said adhesives have the major disadvantage of being mixed with toxic organic solvents (ethyl acetate and
10 isopropanol) which must be evaporated after applying the adhesive composition to its substrate or to the polymer support of the adhesive strip. This operation is inconceivable for dental patients.

Also, the composition disclosed in this patent is difficult
15 to use as such other than in tape or adhesive film form: the immense majority of adhesive applications require a viscous or paste formulation which is much more practical for coating surfaces. Finally, the adhesive strength of the composition previously disclosed does not ensure sufficiently resistant
20 bonding in all cases of utilization.

The purpose of the present invention is to overcome these disadvantages by proposing a photosensitive adhesive composition of polymerizable resin type whose hardening is obtained by polymerization and/or crosslinking.

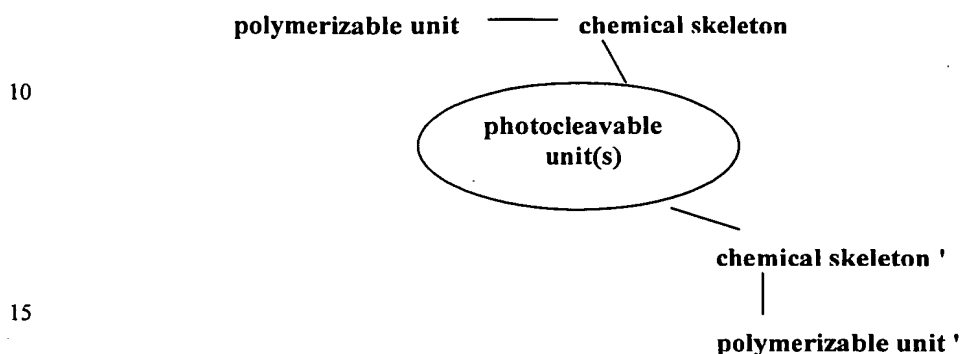
25 For this purpose, and according to the invention, this adhesive composition is remarkable in that it contains:

- means to initiate at least one chain polymerization reaction, to ensure hardening of said composition, and
- a sufficient quantity of at least one bifunctional monomer
30 including firstly a photocleavable centre comprising at least one photocleavable unit, and secondly at least two polymerizable units bound by covalent skeletons to said photocleavable centre and positioned either side of the cleavage site or sites of said photocleavable centre, so that said hardened composition loses
35 its integrity and adhesiveness under the action of uncrosslinking radiation achieving cleavage of the photocleavable units.

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In the remainder of this disclosure, the term monomer shall designate both monomers in the strictest sense and oligomers and prepolymers. Similarly, the term polymerization shall systematically denote "chain" polymerization.

5 According to an essential characteristic of the adhesive composition of the invention, it contains bifunctional monomers whose minimum structure can be described by the following schema:



It can be clearly seen that with the adhesive composition of the invention it is possible to obtain a cross-linked polymer containing "padlocks" in its matrix which are the photocleavable centres. Uncrosslinking actinic radiation will open these padlocks by cleaving the photocleavable units leading to loss of crosslinked cohesion and resulting in loss of adhesiveness, since the polymer disintegrates.

25 According to another characteristic of the composition of the invention, it is in liquid, viscous or paste state at ambient temperature and may also contain chain polymerizable co-monomers which may act as reactive diluent. Therefore, the composition may free from any danger connected with solvent toxicity and is in addition easy to use, its physical properties permitting problem-free coating of the elements to be bonded.

30 Finally, in a preferred variant of embodiment, the initiation means for the chain polymerization reaction are photoinitiators able to initiate the polymerization mechanism under the action of crosslinking radiation whose wavelength λ_1 is different to wavelength λ_2 for uncrosslinking radiation. It will

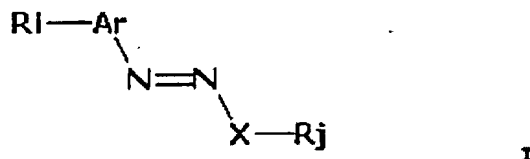
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therefore be understood that with a single lamp and adapted filters, the cement can be polymerized very rapidly (a few minutes) and conversely can be uncrosslinked to separate two elements cemented together by the adhesive composition of the invention.

Other advantages and characteristics will be more readily understood from the following description of several embodiments of the photosensitive adhesive composition of the invention; firstly examples will be given of the families of chemical compounds contained in the bifunctional monomers of the invention with examples of synthesis methods for some of these bifunctional monomers. A description will afterwards be given of the possible applicable variants of the type of initiation means for the polymerization reaction. Finally, compositions preferably intended for clinical dental use will be presented as examples.

According to an essential characteristic of the photosensitive adhesive composition of the invention, it contains bifunctional monomers that are polymerizable and photocleavable. Among all known photocleavable units, consideration will be given to two main families, the aryl-diazos and benzyls.

A first large family of photocleavable units which can be applied is the family of azyl-diazos having the following general structure of formula I:



25

As a general rule, since these compounds are unstable in highly acid or basic media, care is taken that the Ri and Rj substituents do not carry highly acid or basic groups, unless the acidity or baseness is masked by various interactions such as inter- and intramolecular hydrogen bonds for example in the case of acidity or intermolecular bonds existing in the solid state. Also, in the following description of the Ri and Rj substituents, the hydrocarbon groups in particular alkyl, alkoxy, alkylthio,

30

- 5 -

are preferably C1-C6 groups, aryloxy and arylthio are preferably made up of 5 to 14 atoms, preferably 5 to 6 atoms for monomers in their strictest sense, but they may be chains of larger size if oligomers or prepolymers are considered.

5 These aryl-diazo units are therefore represented by the above formula I, in which:

- Ar denotes an aromatic system that is monocyclic or polycyclic, carbocyclic or heterocyclic, including in particular atoms such as S or N, each cycle preferably having 5 or 6 atoms;
- 10 - X denotes an atom chosen from among: C, N, O, P, S;
- Ri is chosen from among the hydrogen, halogen groups, a functional group whether ionic or not (with the exception of halogenated groups able to release strong acids, such as acyl halides), a polymerizable functional group such as those
- 15 described hereafter. The Ri substituent may also be a radical or a hydrocarbon chain which may be aliphatic, acyclic, saturated or unsaturated, straight or branched, a cyclic aliphatic, unsaturated, aromatic or heteroaromatic radical, all these radicals or chains possibly carrying substituents of Ri type or
- 20 interrupted by a heteroatom chosen from among B, N, O, Si, P, S, a halogen or a functional group.

The notion of radical is more appropriate for designating a monomer, whilst the notion of chain is better suited for describing a straight, branched or crosslinked polymer in the

25 entire description of the invention.

On the aromatic cycle of the aryl-diazo unit, the Ri substituents may form between themselves a carbocyclic or heterocyclic cycle, whether substituted or not, preferably comprising no more than 6 atoms to form the cycle; the same

30 applies, as a general rule, to substituents, in particular those defined similarly to Ri which may be located on any radical or hydrocarbon chain mentioned in the entire description of the invention.

Ri may, in particular, be one or more groups of the type:

35 alkyl - straight or branched, saturated or unsaturated, optionally substituted, aryl - aromatic or heteroaromatic,

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substituted or unsubstituted, alcoxy such as methoxy for example or ethoxy, aryloxy, alkylthio, arylthio, benzyl, halogeno, hydroxy, hydroxyalkyl, thiol, alkyloxycarbonyl, aryloxycarbonyl, cyano, carbonyl, formyl, amino, carboxylic and sulfonic ester, 5 carboxylic sulfonic and phosphoric amide, carboxylic sulfonic and phosphoric acid, sulfonate, phosphonate, $-\text{OCONR}'\text{R}''$ group, $-\text{OCO}_2\text{R}'$, $-\text{OSO}_2\text{R}'$, $-\text{OPOOR}'\text{OR}''$, $-\text{R}'\text{NHCOOR}''$, $-\text{R}'\text{OCO}_2\text{R}''$, $-\text{NR}'\text{R}''$ (where R' and R'' represent an alkyl group, a carbocyclic or heterocyclic group, aliphatic, unsaturated, a (hetero-)aromatic 10 group, all substituted or unsubstituted), imine substituted or unsubstituted, nitro, $-\text{N}=\text{N}-\text{R}'$, $-\text{Rp}-\text{Si}-(\text{ORq})_3$ group (in which Rp is a hydrocarbon chain, preferably a straight alkyl chain having at least 3 C atoms, and Rq denotes a hydrogen atom, a hydroxy group, an alcoxy C1-C6 chain, or $-(\text{Si}(\text{ORq}))$ group), a vinyl 15 group, an acrylic group, an alcoxycarbonyl group or an aryltriazene group, among others.

If the aryl group of an aryl-diazo subunit is monocyclic, the substituent Ri donor groups of the aromatic cycle are preferably at para or ortho of the diazo group and the Ri 20 attractor groups preferably at meta of this group.

$-\text{Rj}$ designates one or more substituents, according to the valency of the atom designated by X. Generally, the different Rj are the same or different and may designate an alkyl chain straight or branched, aliphatic or unsaturated, acyclic or 25 cyclic, preferably C1-C6, optionally substituted by substituents meeting the definition of Ri for example optionally interrupted by a heteroatom such as N, O, Si, P, B for example, an aromatic or heteroaromatic group including for example in a preferred chain of 5 or 6 atoms at least one nitrogen or sulfur monocyclic or polycyclic atom, an alcoxy chain, aryloxy chain, a benzyl group, 30 the Rj substituents may also form a cycle preferably having 5 to 6 atoms.

In addition, Rj may evidently be the residue of a chain when the bifunctional monomer compound is of polymer or oligomer 35 size. Finally, Rj may advantageously designate a heteroatom such

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as preferably O, N ou P, structurally arranged with X' in relation to the possibilities offered by the valency of X.

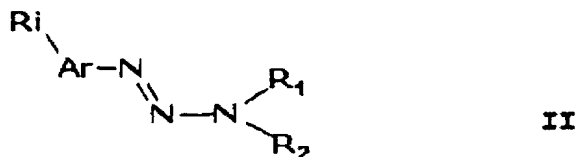
If X is an atom of carbon C or oxygen O (aryldiazoalkyl and aryldiazoether compounds respectively), Rj also designates an alkylthio, arylthio chain, a cyclohexyl, naphthyl group, a hydroxyethyl, cyanoethyl, acryloxyethyl group, alkyl (C1-C6)glycidyl ether or alkyl(C1-C6)vinyl ether, a cyclohexyl epoxy, advantageously in the case of aryldiazoalkyls an attractor group such as a cyano, nitro group, carboxylic, sulfonic and phosphoric acid, carboxylic and sulfonic ester, phosphonate, amide, carbonyl.

If X is an atom of phosphorus P, Rj also advantageously jointly designates the groups or atoms such that they create a photosensitive unit of Ar-N-N-PO(OR')(OR'') arylazophos-phonate type, in which R' and R'' are defined as previously in Ri, in particular R' and R'' may independently designate an alkyl chain whether straight or branched, substituted or not, saturated or not, acyclic or cyclic, carbocyclic or heterocyclic, a (hetero)-aromatic radical, more particularly a hydroxyethyl chain, 1,4- or 1,3-dimethylcyclohexyl, 1,4-dimethylparaphenyl, a methyl, ethyl, propyl, isopropyl, hydroxyethyl, cyanoethyl, acryloxyethyl group, an ether of alkyl (C1-C6)glycidyl or alkyl (C1-C6) vinyl, a cyclohexyl epoxy.

Examples of such compounds can be found for example in the article "New arylazophosphonate-containing Polyurethanes and Polyesters for Laser Ablation Structuring", *Macromol. Mater. Eng.*, 2002, 287, 671-683.

If X is an atom of sulfur S, Rj also advantageously and jointly designates the groups or atoms such as to create a photosensitive unit of AR-N=N-SO(OR')(OR'') arylazosulfonate type, R' and R'' being defined as previously. Rj may also jointly designate the groups or atoms so as to create a photosensitive unit of AR-N=N-SO₂R' arylazosulfone type, or further an Ar-N=N-S-R' arylazosulfide unit.

Finally, if X is an atom of nitrogen N (aryltriazene, arylpentazadiene, arylhexazadiene compounds) consideration is given to the following formula II:

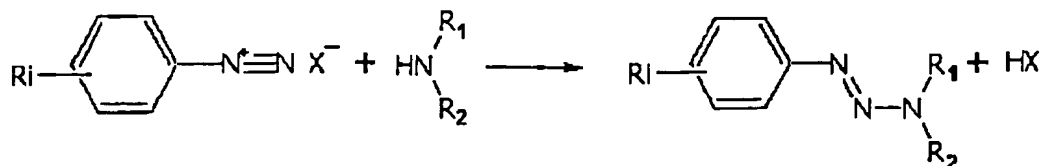


5 in which R_i is defined as previously and the R_1 and R_2
substituents correspond to the definition of R_j .

R1 and R2 may advantageously designate, independently from one another, each of the hydroxyethyl, cyanoethyl, aminoethyl, acryloxyethyl or halogenoethyl groups.

10 R1 and R2 designate the residues of one or two organic compounds, optionally polymers, of which one initially carries at least one primary or secondary amino group at its ends, and independently represent a hydrogen atom (but not the two simultaneously), a functional donor group, an alkyl chain
15 straight or branched, aliphatic, unsaturated, acyclic, cyclic, preferably C1-C6, optionally interrupted by a heteroatom such as N, O, Si, P, B for example, a (hetero)-aromatic group, all these groups or radicals may be substituted by various functional groups such as Ri for example.

20 The same indications as those given above also apply to the
notion of a functional group, with the addition of those
concerning the synthesis of the triazene unit. The synthesis
schematic of these units is based on (mono/bi)-coupling between a
diazonium salt of an aromatic amine and another amine defined by
25 the formulas NHR_1R_2 or NH_2R_1 and, in the case of monocoupling, is:



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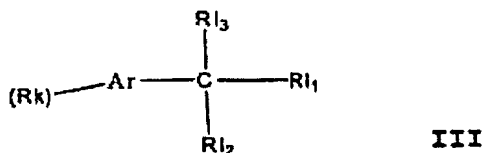
The R_1 and R_2 substituents are preferably such as the NHR_1R_2 or NH_2R_1 amine exists in this form or other form in which it is stabilized or made reactive, such as hydrates, ammonium chlorides for example. Preferably R_1 and R_2 do not designate halogens.

5 Similar to R_i , R_1 and R_2 may represent the necessary atoms to complete a cycle. In the composition of the invention use may be made in particular of aryl-triazene compounds or derivatives in which R_1 and R_2 are for example a $-N=N-R'$ group, $-NR'-N=NR''$ group, OR group, $NR'R''$ group (R' and R'' have the meanings
10 previously given), an alkyl group such as methyl, ethyl, propyl, isopropyl, butyl, tert-butyl, an alkoxy group substituted or unsubstituted, a benzyl group, a (hetero)-aromatic group, all substituted or not by substituents of R_i type, a hydroxyethyl, cyanoethyl, aminoethyl, acryloxyethyl or halogenoethyl group.

15 Persons skilled in the art will find examples of aryl-triazene compounds applicable to the adhesive composition of the invention in the publications by Oskar Nuyken and/or his team.

 Finally, the photocleaving site of the aryl-diazos is generally the $-N=N-X-$ chain of which at least one of the bonds is
20 broken under $\square 2$ actinic radiation; in the bifunctional monomers corresponding to the invention, the chemical skeletons binding said unit to the polymerizable units are therefore reasonably arranged either side of the $-N=N-X$ chain.

25 A second large family of photocleavable units applicable to the adhesive composition of the invention is the benzyl family, having the following general structure of formula III:



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 Generally, as for the aryl-diazos, the alkyl, alkoxy, alkylthio substituents are preferably C1-C6, aryloxy and alkylthio preferably have 5 to 14, further preferably 5 to 6

- 10 -

atoms but they may be chains of larger size. Also the R_k, R_l, R_m substituents described below may evidently be the residue of a chain when the bifunctional monomer compound is of oligomer polymer size.

5 These benzyl units, which have better stability in acid medium than the aryl-diazos, are therefore represented by formula III above, in which:

 - Ar designates an aromatic or heteroaromatic radical (including an atom such as N or S for example), monocyclic or
10 polycyclic, carrying at least one R_k substituent different to the benzyl substituent explicitly present (nitro for example if nitrobenzyls are considered),

 - R_k is generally one or more substituents of the aromatic cycle, and designates an auxochromic or bathochromic substituent
15 possibly chosen from among the following examples: hydrogen, halogen, alkyl chain, aliphatic, acyclic saturated or unsaturated, straight or branched, a cyclic radical whether aliphatic, unsaturated, aromatic or heteroaromatic (these chains and radicals may be substituted, interrupted or terminated by a
20 heteratom such as B, N, O, Si, P, S or a halogen), a nitro, cyano, alcoxy, aryloxy, alkylthio, arylthio, benzyl, arylalkyl, hydroxy, thiol, alkyloxycarbonyl, aryloxycarbonyl, carbonyl, formyl, amino group, carboxylic and sulfonic ester, carboxylic sulfonic and phosphoric amide, carboxylic sulfonic and phosphoric
25 acid, sulfonate, phosphonate, a -OCONR'R'', -OCO₂R', -OSO₂R', -OPOOR'OR'', -R'NHCOOR'', R'OCO₂R'', NR'R'' group (R' and R'' are an alkyl, aryl group, a carbocyclic or heterocarbocyclic group), imine substituted or unsubstituted, diazo -N=N-R', a -R_p-Si-(OR_q)₃ group (R_p and R_q as defined for the aryl-diazos), ether of
30 alkyl(C1-C6)glycidyl or alkyl(C1-C6)vinyl, cyclohexyl epoxy.

 - R₁₁/R₁₂/R₁₃ designate a hydrogen, an alkyl, alcenyl, alcynyl, alkylaryl chain, substituted or unsubstituted, preferably C1-C6, a carbocyclic or heterocyclic chain, saturated or unsaturated, aromatic or heteroaromatic, substituted or not,
35 preferably having 5 to 6 atoms, an alcoxy, aryloxy, alkylthio, arylthio chain, an alkyloxycarbonyl group, -NR'COR'' group, -

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OCOR' group, -OCOOR' group, -OCONR'R'' group, NR'COOR'' group, -OPOR'R''R''' group, -OSO₂R' group, -OPOOR'OR'' group, -NR'R'' group, -COOR' group, -CONR'R'', SOOR', -COR' group (R', R'', R''' have the previously indicated denotations), an imine group substituted or not, hydroxy, thiol, a carboxylic acid or derivative, a halogen, nitrile, an alkyl(C1-C6)glycidyl or alkyl(C1-C6)vinyl ether, cyclohexyl epoxy, -Rp-Si(ORq)₃ group (Rp and Rq as defined previously).

Persons skilled in the art will for example find examples of compounds meeting the definition of formula III in the publication "Photosensitive protecting groups" *Israel J. of Chem.*, 1974, 12(1-2), pp. 103-113.

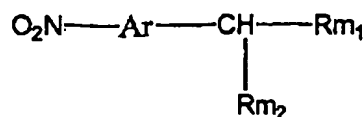
Generally, the photocleaving site of benzyls is the benzyl carbon explicitly present in formula III of which at least one of the bonds with one of the R₁₁/R₁₂/R₁₃ groups is ruptured under λ 2 actinic radiation; in the corresponding bifunctional monomers of the invention, the chemical skeletons binding said unit to the polymerizable units are therefore reasonably arranged either side of the benzyl carbon under consideration.

One category of benzyl units applicable to the invention which is particularly efficient and does not comprise any nitro function explicitly at the ortho position of the benzyl function, are the benzyl units in which Ar is at least bisubstituted at the meta of the benzyl function by an alcoxy or aryloxy chain and in which two of the R₁₁/R₁₂/R₁₃ substituents are a hydrogen atom or an alkyl group, preferably C1-C4, preferably at least one of the two substituents being an alkyl group, while the last substituent is a chain starting with a heteroatom such as O or N for example or a functional group of ester or carbamate type.

Also, the best preferred forms of these benzyl units are the 2-nitrobenzyl derivatives, of which some are given in patents US 5 600 035 and US 6 100 008, which can be given by the following general formulas:

• Formula 1:

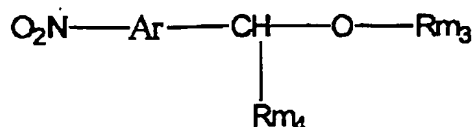
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in which:

- AR is as previously defined;
- 5 - R_{m1}/R_{m2} are defined as R₁₁/R₁₂/R₁₃.

• Formula 2:

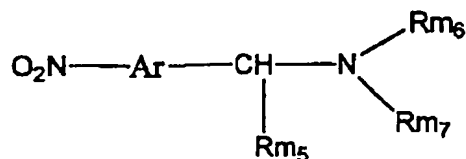


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in which:

- Ar is defined as previously,
- R_{m4} is defined as R₁₁/R₁₂/R₁₃,
- R_{m3} is defined as a hydrogen, an alkyl, alkenyl, alcyanyl,
- 15 alkylaryl chain, substituted or not, interrupted by a heteroatom
such as N, O, P, Si, S, preferably C1-C6, a carbocyclic or
heterocyclic chain, (un)saturated, (hetero)-aromatic, substituted
or not, preferably 5 to 6, an alkyloxycarbonyl group, POR'R''R'''
group, -SO₂R' group, -POOR'OR'' group, -COOR' group, -CON'R'', a
- 20 COR' group (R', R'' and R''' having the denotations given
previously for R' and R''), alkyl(C1-C6)glycidyl or alkyl(C1-
C6)vinyl ether, cyclohexyl epoxy, (Rp-Si(ORq)₃ group (Rp and Rq
as previously defined).

25 • Formula 3:

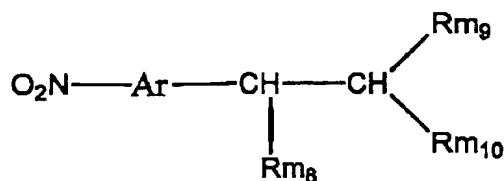


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in which:

- Ar is defined as previously,
- R_{m5} is defined as R₁₁/R₁₂/R₁₃,
- 5 - R_{m6}/R_{m7} are defined as a hydrogen, an alkyl, alkenyl, alcyanyl, alkylaryl chain, substituted or not, interrupted by a heteroatom such as N, O, P, Si, S, preferably C1-C6, a carbocyclic or heterocyclic chain, (un)saturated, (hetero)-aromatic, substituted or not, preferably having 5 to 6 atoms, an
- 10 alkyloxycarbonyl group, -R'COR'' group, R'COOR'' group, R'R'', -COOR' group, -CONR'R'', a COR' group (R' and R'' having the denotations previously given), a hydroxy group, alkyl(C1-C6)glycidyl ether or alkyl(C1-C6)vinyl ether, cyclohexyl epoxy, -
- 15 Rp-Si(ORq)₃ group (Rp and Rq as defined previously).

• Formula 4:



20 in which:

- Ar is defined as previously,
- R_{m8}/R_{m9}/R_{m10} are defined as R₁₁/R₁₂/R₁₃.

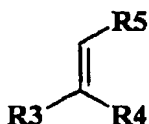
25 Among all the photocleavable units presented above, particular preference is given to arylazophosphonates, arylazosulfonates, arylazosulfides, aryltriazenes and 2-nitrobenzyls for their proven cleaving efficacy, the involved wavelengths, their stability in the adhesive composition of the invention and more particularly, for the 2-nitrobenzyls, their

30 commercial availability and their better stability in acid medium, which may prove to be essential in some considered applications.

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According to an essential characteristic of the invention, the bifunctional monomers used contain units that are polymerizable through chain polymerization reaction. This reaction may be conducted by three processes well known to persons skilled in the art: radical, cationic or anionic.

In a first variant the polymerization process is radical. The polymerizable units selected for radical polymerization are vinyl units. These are described as follows:



IV

10

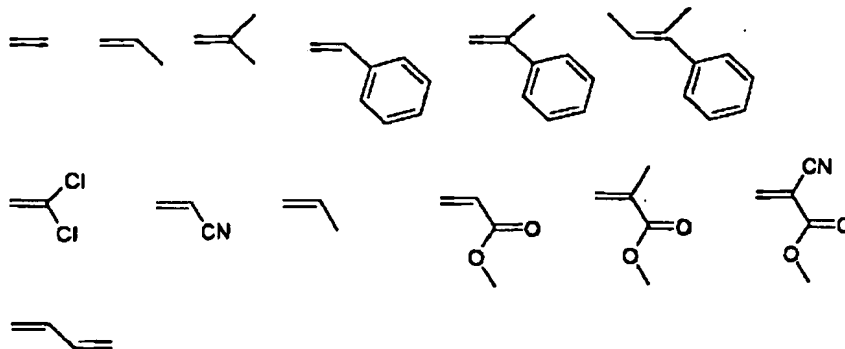
in which R₃, R₄ and R₅ are substituents able to activate together the double vinyl bond vis-à-vis radical addition chain reactions. At least one of these substituents is a hydrocarbon chain, optionally interrupted by a functional group such as Ri or a heteroatom such as N, O, Si, P, S substituted or not by groups such as Ri, linked to at least one photocleavable unit so as to meet the structural criteria of the bifunctional monomers of the invention. More generally, R₃ or R₄ or R₅ may represent a hydrogen atom, a halogen atom, a functional group, an alkyl, alkoxy, chain saturated or unsaturated, substituted or not, preferably C1-C6, or an aryl, aryloxy group substituted or not preferably having 5 to 6 atoms, an attractor functional group such as a carbonyl group, a carbonyloxyalkyl or carbonyloxyaryl group, an amide group, cyano group, optionally a sulfonic carboxylic acid group, and their salts, with optional appropriate restrictions or exclusions to preserve compatibility with the photocleavable units, or further an alcoxycarbonyl group.

To obtain good reactivity in respect of radical polymerization, persons skilled in the art may, without limiting the invention, select at least one of the substituents from among the cited attractor groups to create (meth-)acrylic units for example.

30

- 15 -

As non-restrictive examples, below are given some structures which require structural modification for their linking to a photocleavable unit using one of the methods explained below or using techniques known to persons skilled in the art:



In one alternative embodiment of the composition of the invention, electron acceptor vinyl units may coexist in the composition that are able to create a charge transfer complex with at least one other complementary partner, this other partner itself, in a certain number of cases, possibly being a vinyl unit that will be an electron donor. The charge transfer complex is then able to initiate the radical polymerization reaction under radiation of wavelength λ_1 . In particular, it is possible to choose an electron donor unit from among the following examples: styrene, cyclohexane oxide, vinyl acetate, vinyl ether, phenyl glycidyl ether, exomethylene dioxolane such as 4-methylene-2-phenyl-1,3-dioxolane, alkyl methacrylate, vinyl pyrrolidone, and an electron acceptor unit among the following examples: maleic anhydride, acrylonitrile, diethyl fumarate, fumaronitrile, maleimides.

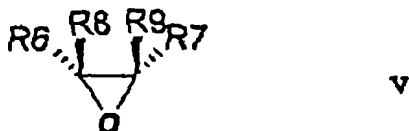
In the second variant of polymerizable units applicable to the composition of the invention, the polymerization process is cationic. A cationically polymerizable unit is a unit which polymerizes or crosslinks in the presence of an acid or cation.

Such units may be chosen from among the following families: epoxide (or oxirane), oxetane, oxolane, cyclic acetal, cyclic lactone, thiirane, thietane, vinyl ether, cyclic ether, cyclic

- 16 -

thioether, spiroorthoester, spiroorthocarbonate, aziridine, siloxane, styrenes.

With a view to photoinduced polymerization in particular (cf. description of initiating means hereafter), preference is given to oxirane units whose structure is defined by following formula V:



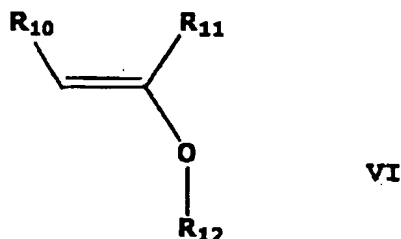
in which R_6 , R_7 , R_8 , R_9 are the same or different, at least one of the substituents R_6 , R_7 , R_8 , R_9 being a hydrocarbon chain, and generally represent an atom of hydrogen, halogen, an alkyl, alkoxy, alkylthio chain, straight or branched, saturated or unsaturated, acyclic or cyclic, preferably C1-C6, optionally substituted, optionally interrupted by a heteroatom, an aromatic or heteroaromatic aryl group, an aryloxy or arylthio group preferably having 5 to 6 atoms, a benzyl group, an imine group, $NR'R''$ amino $NR'R''$, $SiR'R''R'''$, alkyl(C1-C6)oxycarbonyl, aryl(C1-C6)oxycarbonyl, amide, carboxylic and sulfonic ester, sulfonate, phosphonate, a carbonyl, cyano group, $-CONR'R''$ group, $-OCO_2R'$, $-OSO_2R'$, $-OPOOR'OR''$, $-R'NHCOOR''$, $R'OCO_2R''$ in which R , R' , R'' represent an alkyl group (preferably C1-C6) substituted or not, aryl (preferably with 5 to 6 atoms), a carbocyclic or heterocyclic group, aliphatic, unsaturated or aromatic, substituted or unsubstituted.

Advantageously, for reasons of steric hindrance, two of the substituents R_6 , R_7 , R_8 , R_9 are a hydrogen atom.

Typical derivatives are for example the derivatives of diglyceride ether or of 3,4-epoxycyclohexyl.

A further particularly preferred family of units, with a view to photo-induced cationic polymerization, is the family of units of vinyl ether type whose structure is defined by formula VI:

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in which:

- R10 and R11 are the same or different and designate a
5 hydrogen atom or advantageously a straight or branched C1-C6
alkyl chain, substituted or not, saturated or unsaturated,
acyclic or cyclic, optionally interrupted by a heteroatom such as
O, N, Si, P for example, an aromatic or heteroaromatic aryl group
(preferably having 5 to 6 atoms), an alkoxy chain (preferably C1-
10 C6), an alkylthio chain (preferably C1-C6), arylthio (preferably
having 5 to 6 atoms);

- R12 advantageously designates a straight or branched C1-
C6 alkyl group, substituted or not, saturated or unsaturated,
acyclic or cyclic, optionally interrupted by a heteroatom such as
15 O, N, S, Si, P for example, an aromatic or heteroaromatic aryl
group (preferably having 5 to 6 atoms).

Finally, among other examples of ethylene functions that
are cationically polymerizable, a choice may be made from among
styrene derivatives in particular such as styrene, para-
20 alkoxy styrene derivatives, para-chloromethylstyrene, vinyl
toluene, α -methylstyrene.

In a third variant, polymerization is anionic. Among the
anionically polymerizable units, units of vinyl type may be
chosen (according to formula IV) but which carry electro-
25 attractor substituents such as carboxylic ester in particular
(methacrylic derivatives for example), or cyano, or which carry
substituents permitting strong positive polarization of the
carbon at β of the double bond when approaching the nucleophilic
species, such as is the case for example with units of butadiene,
30 styrene, vinylpyridine type.

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Heteroaromatic cycles may also be chosen such as those described for cationic chain polymerization, in particular oxirane, thiirane, lactones, lactames.

5 A method is described below for preparing bifunctional monomers grouping together the minimum structural criteria required for producing a photosensitive adhesive composition of the invention. This method comprises several steps, namely a first step to produce a photocleavable unit or group of units of
10 aryl-triazene or 2-nitrobenzyl type, optionally followed by a structural arrangement step of the skeleton of the photocleavable unit, and a last step during which this photocleavable unit is attached to one or more polymerizable functions via a chemical skeleton.

15

I - FIRST STEP: SYNTHESIS OF PHOTOCLEAVABLE UNITS

Case 1: Fabrication of an aryltriazene unit.

Two principal implementation modes can be considered.

20 1. -First implementation embodiment

1°) Firstly diazotization is conducted of an arylamine (this term encompasses (hetero)-aromatic structures optionally pluri-substituted by -NH₂ amino groups without excluding any other substituent of Ri type, such as defined above) in a non-
25 oxidizing aqueous acid medium to form the corresponding diazonium salt. Diazotization is achieved by dissolving the arylamine in an aqueous mineral acid, such as concentrated HCl or H₂SO₄ for example, and adding thereto, at a temperature of between -10° and 30°C, an aqueous solution of nitrite ions. The solution of
30 diazonium salt obtained is then used either as such, or after modification using known means for the preparation of the diazonium salt of arylamine with a different anion, as is the case if a diazonium chloride is cold precipitated through the addition of an appropriate quantity of tetra-hydroborofluoric
35 acid (HBF₄). In similar manner, salts of hexafluorophosphate can

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be prepared (anion PF_6^-), of tetra(pentafluorophenyl)-borate (anion $\text{B}(\text{C}_6\text{F}_5)_4^-$), or salts of hexafluoroantimonate (anion SbF_6^-).

2°) The diazonium salt, in its initial or "exchanged" form, is then dissolved in an aqueous solution, over the same
5 temperature range as previously, and the pH is adjusted in an alkaline range to achieve diazoic mono-or bi-coupling with at least one of the primary or secondary amino sites of an organic compound.

For this purpose, the compound carrying amino groups is
10 dissolved in an aqueous solution, preferably of pH 7 to 8, or in an organic solvent (alkane, THF, acetonitrile) to which is added a diazonium salt at a temperature of between -10°C and $+30^\circ\text{C}$.

At the end of the reaction, the triazene compound obtained is isolated using any known technique depending upon chemical
15 structure. In a biphasic medium the products may be isolated by simple filtration, otherwise the products may be subsequently purified for example by re-crystallization and column chromatography.

20 2. - Second implementation embodiment

Another preparation method consists of obtaining a diazonium salt from an arylamine able to undergo diazotization in an organic medium such as ethyl ether, THF for example or dry halogenated solvents such as dichloromethane or chloroform.
25 Diazotization is conducted at a temperature of between -50°C and $+30^\circ\text{C}$ by adding to a solution of arylamine with a Lewis acid such as BF_3 , PF_5 , SbF_5 for example, a solution of organic nitrite such as tert-butyl nitrite for example. The salt is then extracted using conventional means, in particular by washing and filtering.

30 Diazoic coupling is then performed by adding to the recovered diazonium salt, dissolved in an inert dispersing solvent, a solution of an organic compound carrying at least one primary or secondary amino group, this reaction being conducted at a temperature of between -50°C and $+50^\circ\text{C}$ in the presence of a
35 base which is preferably sodium or potassium carbonate. The aryl-triazene unit obtained is isolated using known techniques. It is

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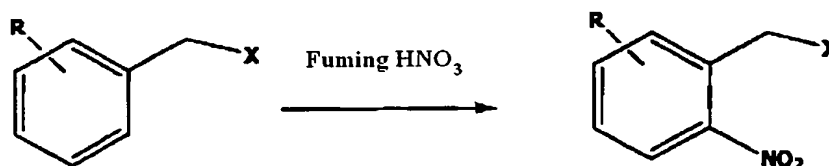
to be noted that only the diazotization method undergoes change, diazoic coupling also possibly being conducted as indicated under I.1.2°).

5 Case 2: Fabrication of a 2-nitrobenzyl unit

The synthesis variants are numerous, two important distinctions exist depending on whether the nitration of an aromatic cycle is necessary or not to arrive at a specific 2-nitrobenzyl structure (this depends upon source commercial products).

1. First implementation embodiment: nitration

1°) A first structure type is created by nitrating benzyl compounds substituted in a form able to promote nitration at least at the ortho position of the benzyl group. Said nitration can be conducted under conditions known to persons skilled in the art, which are the use of dilute or concentrated nitric acid, either alone or combined with concentrated sulfuric acid, acetic anhydride or the use of a nitronium salt (NO_2BF_4 , $\text{NO}_2\text{CF}_3\text{SO}_3$ for example in aprotic organic solvents), or of nitrites (for example NaNO_2 in the presence of trifluoroacetic acid), or esters of nitric acid (ethyl nitrate for example used under alkaline conditions or with a Lewis acid), or N_2O_5 in CCl_4 in the presence of P_2O_5 in an anhydrous medium under conditions of temperature or time suitable for the reactivity of the aromatic cycle.



X = halogen, OH...

2°) A second type of structure is created by nitrating benzene compounds of which at least one nitratable position is adjacent to a precursor function of a substituted methylene.

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Among these functions, the reducible functions (aldehyde, ketone, amide, carboxylic acid, nitrile, imine, hydrazone, oxime, epoxide..) are preferred functions, the reducing of said function to be conducted under conditions in which an aromatic nitro group is preserved; therefore the concomitant use is excluded of metals and acid (for example Zn and HCl), of catalytic hydrogenation conditions, of $\text{AlH}_3\text{-AlCl}_3$, TiCl_3 , LiAlH_4 , $\text{NaBH}_4 + \text{NiCl}_2 (\text{PPh}_3)$, $\text{NaBH}_4 + \text{CoCl}_2$.

10 2. Second implementation embodiment: no nitration

A third type of structure is created by modifying o-nitrotoluene derivatives. Suitable techniques known to persons skilled in the art are bromation of an o-nitrotoluene for example in the presence of N-bromosuccinimide or the treatment in polar organic solvent (such as DMSO for example) of derivatives of o-nitrotoluene with paraformaldehyde in the presence of strong bases (such as KOH, tertibutylate potassium, Triton B, DBU, guanidines for example) to arrive at derivatives of 2-(nitrophenyl)ethyl.

20

II- SECOND STEP: STRUCTURAL ARRANGEMENT

Generally, when the skeleton of the photocleavable unit obtained after the first step has functions capable of directly fixing a polymerizable unit such as defined in the invention, it is not essential to modify the chemical structure of this skeleton, and in this case this step is omitted to pass directly to step three. If not, persons skilled in the art are able to implement the necessary reactions to achieve fixing of this polymerizable unit during the third step of the method.

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III- THIRD STEP: ASSOCIATION OF POLYMERIZABLE UNITS WITH PHOTOCLEAVABLE UNITS

Case 1: Polymerizable units of VINYL type

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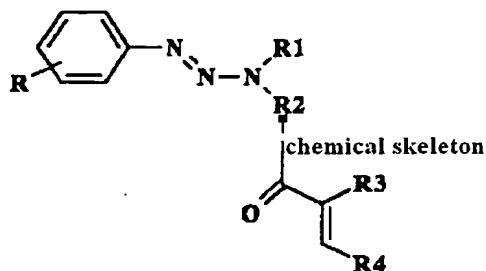
Here consideration will be given to all the vinyl units previously described, namely those that can be radically polymerized (formula IV), cationically polymerized (vinyl ethers of formula VI and styrene derivatives) or anionically
 5 polymerized.

Starting with the chemical structure surrounding the photocleavable unit or units, there are two variants for associating vinyl units with photocleavable units. A first variant to elongate the skeleton and include therein one or more
 10 vinyl polymerizable functions, is a process during which the vinyl function is created.

The other variant consists of grafting pre-existing vinyl units.

15 1°) First variant: creation of the vinyl function

This preferably involves creating a vinyl function of acryloyl type illustrated below in the case of a photocleavable unit of aryl-triazene type.



20

This variant for creating the acryloyl function consists of using a reaction of nucleophilic substitution type on an acryloyl carbon. Different nucleophilic agents can be used, a distinction
 25 being made if necessary between possibilities applicable to aryl-diazos, in particular arylazophosphonates and aryltriazenes, and to benzyls in particular 2-nitrobenzyls.

1°)1) The nucleophilic agent is an O-R group as is the case for:

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a) attack by an alcohol or alcoholate on acryloyl halides, preferably conducted in the presence of a base such as pyridine;

b) attack by an alcohol on an acryloyl anhydride, preferably catalyzed by a base such as pyridine or 4-(N,N-dimethylamino)pyridine (DMAP);

c) attack by an alcohol on an acrylic acid.

• for aryl-diazos: esterification reactions abound in the literature and persons skilled in the art may refer thereto with the reservation that esterifications are excluded which are conducted under conditions of acid catalysis. The preferred conditions include activations of acid functions into ester functions of 2-pyridinethiol, in the presence of 1-methyl-2-chloropyridinium iodide, in the presence of dehydrating agents particularly chosen from the group: dicyclohexylcarbodiimide (DCC), diisopropylcarbodiimide (DIPC) combined with 4-methylamino-pyridinium tosylate (DPTS), N,N'-carbonyldiimidazole, 1,1'-carbonylbis(3-methylimidazolium), alkylchloroformate and triethylamine, di-2-pyridylcarbonate, di(2-pyridyl)-dithiocarbonate, 1-hydroxybenzotriazole, penta-fluorophenyl diphenylphosphate, diethylazodicarboxylate and triphenyl phosphine, Amberlyst-15,

• for benzyls: on account of their better stability in acid medium, in addition to the attack methods given above for aryl-diazos, well-known methods may be used such as acid catalysis (H_2SO_4 , sulfonic para-toluene acid), distillation and/or azeotropic distillation.

d) attack by an alcohol on an acrylate (transesterification reaction):

• for aryl-diazos: the embodiments containing acid catalysis are to be excluded: on the other hand, the preferred treatment modes include transesterification reactions in the presence of catalysts such as titanates, tin oxides and esters such as $\text{Bu}_2\text{Sn}(\text{OMe})_2$, $(\text{Bu}_2\text{SnCl})_2\text{O}$, dibutyl tin dilaurate, $\text{BuSn}(\text{O})\text{OH}$, or further $\text{Zn}(\text{CH}_3\text{COO})_2$. Consideration may also be given to conditions of basic catalysis in the presence of triethylamine or 1,8-diazabicyclo[5.4.]undec-7-ene;

- 24 -

- for benzyls: in addition to the reactions set forth above, transesterifications under acid catalysis are possible; as catalyst, special mention is made of sulfonic para-toluene acid, sulfuric acid, boric acid, (pyro)phosphoric acid, phosphonic acid, exchange resins such as DOWEX 50X2-100.

1°)2) The nucleophilic agent is an -OCOR oxycarbonyl group, as is the case for:

the attack by salts of carboxylic acids on acryloyl halides in the presence of pyridine or triethylamine or of exchange resins carrying tertiary amino or quaternary ammonium groups, of Lewis acids such as FeCl_3 , AlCl_3 or a combination of these elements.

1°)3) The nucleophilic agent is a -S-R group, according to embodiments similar to embodiments 1°)a), 1°)b), 1°)c) and 1°)d).

1°)4) The nucleophilic agent is a NR_2 group as is the case for:

- a) attack by an amine according to an embodiment 1°)a);
- b) attack by an amine according to an embodiment 1°)b);
- c) attack by an amine according to an embodiment 1°)c), in particular the embodiments in the presence of a dehydrating agent such as salts of pyridinium, of Bu_3N , or reactions conducted in the presence of $\text{Ti}(\text{OBu})_4$;

- for benzyls: consideration may also be given to hot treatment with acrylic acid in the presence of amides of carboxylic or sulfonic acids, treatment in the presence of trialkylaminoborane, in the presence of Lewis acids in particular such as FeCl_3 , ZnCl_2 , potassium, sodium or ammonium dihydrogen phosphate, $\text{BF}_3\text{-Et}_2\text{O}$;

d) attack by an ammonium salt of a primary amine with an acrylamide optionally in the presence of complexing agents such as BF_3 ;

e) attack by an amide on an acryloyl halide in the presence of a base such as pyridine.

- 25 -

1°)5) The nucleophilic agent is a -NHCOR group as is the case for attack by an amide on an acryloyl halide according to an embodiment 1°1)a).

5 2°) Second variant: grafting of vinyl units

In some embodiments of the invention, the polymerizable vinyl unit is already present in its appropriate form in the molecule which grafts itself onto the photocleavable unit.

For this purpose, depending upon the type of vinyl unit,
10 various methods may be used. However, having regard to the first mode of attachment of the acrylic function described above, the invention comprises a general mode for grafting the vinyl function via all the mechanisms set forth in the first mode of attachment, during which the acrylic function was created. This
15 general mode assumes the reaction between a molecule or an organic macrochain preferably having at one or more of its ends one or more vinyl functions in a form that is the same as the one located within the desired structure of the photosensitive monomer, and having at another end a reactive F1 function and a
20 molecule or pre-synthesized macrochain carrying one or more aryl-diazo or benzyl units linked by various chemical skeletons, and on at least one end a reaction function F2. (F2 is antagonist of F1 according to the first mode of attachment of an acrylic function, i.e. under the conditions described above, F1 and F2
25 may react to form a covalent F1-F2 bridge).

A molecule including an aryl-triazene unit, linked by a suitable chemical skeleton to a -OH hydroxyl function, can for example be caused to react with a molecule having on its ends a polymerizable olefin function and a carboxylic acid function in
30 the presence of a carboxylic acid function activator (DCC) used to graft the carboxylic acid onto the hydroxyl function.

In addition to all the grafting modes derived from the mechanisms described above under 1°) for the first attachment mode of the acryloyl function, two other types of reactions may
35 be added.

- 26 -

2°)1) Formation of carbamate type links, as is the case for:

a) attack by a nucleophil on an isocyanate or isothiocyanate, giving urethane or urea links for example in the case of attack on an isocyanate by an alcohol or an amine respectively. Said reaction may be commonly catalysed by catalysts such as DABCO or metal-containing catalysts such as: $\text{Bu}_2\text{Sn}(\text{OMe})_2$, dibutyl tin dilaurate, $\text{BuSn}(\text{O})\text{OH}$ or $\text{Zn}(\text{CH}_3\text{COO})_2$ for example.

b) The reaction of phosgene derivatives, such as a ROCOCl chloroformate on an alcohol or an amine or another nucleophilic group. In this case a carbonate or urethane may be obtained according to a preferred nucleophilic catalysis mode as in 1°)b).

c) Reactions of transesterification type conducted between a nucleophilic attacker of alcohol or amine type for example on a carbamate precursor of phenylcarbonate or phenylurethane type for example, said reaction being preferably catalyzed in the presence of a catalyst of the type cited previously under 2°)1)a).

2°)2) Formation of β -hydroxyester links

such as those obtained in particular by nucleophilic attack by a carboxylate anion on an oxirane; this reaction preferably being conducted under nucleophilic catalysis in the presence of catalysts such as triethylamine, N-methylmorpholine, N-methylpyrrolidine, N,N-dimethylbenzylamine, ion exchange resins carrying tertiary amine or quaternary ammonium sites and more particularly referenced as weak and/or strong base anion exchange resins such as Dowex 44, these catalysts being used either alone or in the presence of co-catalysts such as a Lewis acid, for example FeCl_3 or CrCl_3 , or of $\text{Zn}(\text{OOC-C}_7\text{H}_{15})_2$ or $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ type, however acid catalysts may be considered for o-nitrobenzyls (for example trifluoroacetic acid).

CASE 2: Polymerizable units of OXIRANE type

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Here consideration will be given to all the above-described oxirane units, namely those which can be cationically polymerized (formula V) and anionically polymerized.

As for the vinyl units, the two variants for linking an oxirane unit to a photocleavable unit are either the creation of an oxirane unit on the skeleton of the photocleavable unit, or grafting.

1°) First variant: creation of an oxirane function

One first way of creating an oxirane function consists of treating a halohydrine function according to a nucleophilic substitution method of second order, using a base such as NaOH for example in the presence of water or dimethylsulfoxide for example. The dehydration may also be performed of a 1,2-diol function by treatment with DMF dimethylcetal or diethyl azodicarboxylate in the presence of PPh_3 .

A second method, preferably applied to units of benzyl type for which it is a method of choice, consists of epoxidation of an olefin in the presence of a peroxydic reagent, among which preference is given to m-chloroperoxybenzoic acid or 3,5-dinitroperoxybenzoic acid. The use of hydrogen peroxide or tert-butyl hydroperoxide in the presence of an alkaline solution or the use of Triton B ($\text{PhCH}_2\text{N}^+\text{Me}_3\text{OH}^-$) is also a preferred manner for benzyl or aryltriazene substrates, or further the treatment of olefins with an alkyl peroxide and catalyzed by a Vanadium, Titanium or Cobalt complex. For benzyl units having at one end of the chemical skeleton a unit of allylic alcohol type, it is possible to conduct synthesis of an oxirane function in the presence of tert-butyl hydroperoxide, titanium tetraisopropoxide and a dialkyl tartrate under Sharpless conditions, or further with the combination of Re_3O /bis(trimethylsilyl) peroxide/ H_2O_2 .

A third manner applicable to benzyl and aryldiazo photocleavable units is the treatment of an alcoholate or phenate, generated at one end of the skeleton linked to the photocleavable unit, with an epihalohydrine or any similar derivative. A derivative method is treatment of a carboxylic

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acid, or preferably its salt - sodium for example, or any other equivalent function such as sulfonic acids for example, with an epihalohydrine in the presence of quaternary ammonium salts for example such as benzyltrimethylammonium chloride or further in
5 the presence of ion exchange resins referenced as weak base/high base anion exchange resins.

A fourth manner applicable to photocleavable benzyl and aryl diazo units, preferably to aryl triazenes, is treatment of an aldehyde or ketone having at least one end of the skeleton linked
10 to the photocleavable unit by a sulfur ylide such as dimethyloxosulfonium methylide or dimethylsulfonium methylide.

2°) Second variant: grafting of oxirane units

Several, non-limitative, examples are given below to
15 conduct this grafting.

One first example, set forth above under 1°) but applicable here since it involves destruction of an oxirane function, that is present on a reagent, for its subsequent re-creation during the reaction, is the treatment of an alcoholate or phenate,
20 generated on at least one end of the skeleton linked to the photocleavable unit, with an epihalohydrine. The alcoholate may be generated for example in the presence of sodium hydride or by using solutions, in particular aqueous solutions of NaOH or KOH, in the optional presence of a tertiary amine (for example
25 triethylamine, tributylamine) or an ammonium salt (tetrabutylammonium bromide for example) or an ion exchange resin. A derivative method is the treatment of a carboxylic acid or preferably its salt, sodium for example, or any other equivalent function such as sulfonic acids for example, with an
30 epihalohydrine in the presence of quaternary ammonium salts for example, such as benzyltrimethylammonium chloride, or of ion exchange resins referenced as weak base/strong base anion exchange resins.

A second method consists of treating an alcohol with
35 epichlorohydrine, or any epihalohydrine or any 1,2-epoxy derivative, in the presence of a catalyst of aluminium

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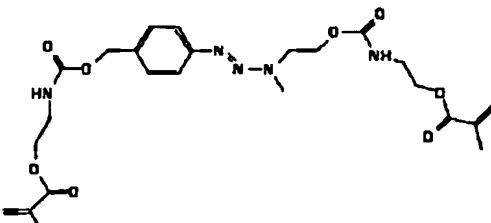
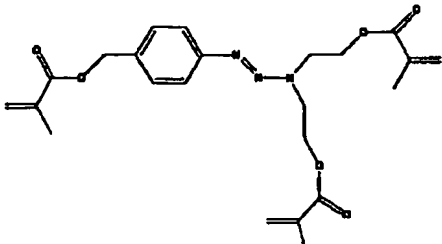
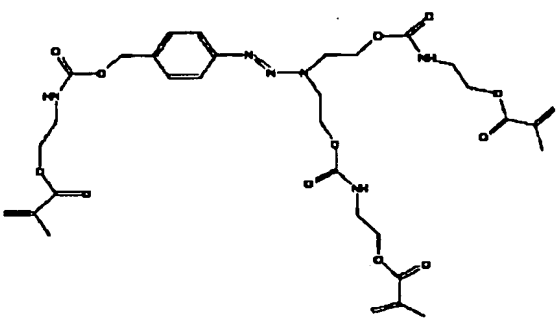
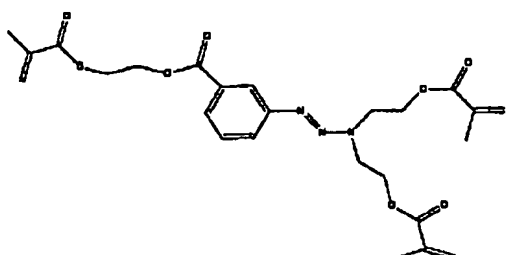
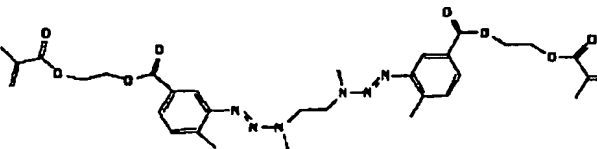
trialkoxide type, preferably C1-C4, or of aluminium isopropoxide type for example and of an acid co-catalyst such as H₂SO₄ for example followed by removal under alkaline conditions.

A third manner is the treatment of an alcohol with an
5 epihalohydrine in the presence of ZnCl₂/H₂SO₄ or ZnCl₂/BF₃.Et₂O followed by removal under alkaline conditions. SnCl₄ or BF₃.Et₂O are also reagents which can be used under similar conditions.

A fourth manner is the treatment of benzyl halide groups
(carried by the skeleton of the photocleavable unit) with glycol
10 or its derivatives in the presence of a hydride, in particular sodium hydride, in a solvent such as THF, acetonitrile or DMF, optionally in the presence of a quaternary ammonium salt such as tetrabutylammonium iodide for example.

Below are given some examples of bifunctional monomers
15 incorporating photocleavable and polymerizable units which meet the above cited definitions and are synthesized according to any of the aforesaid techniques.

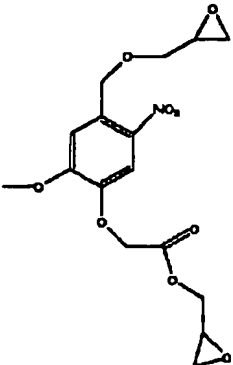
| Structure | Name | Ref |
|-----------|---|-----|
| | 1,2-Bis[1-(4''-methacrylatemethyl)-phenyl-3-methyl]triaz(1)ene-ethane | AT1 |
| | 1,2-Bis[1-(4'-(methacrylate-ethyl)aminocarbonyloxymethyl)phenyl-3-methyl]triaz(1)ene-ethane | AT2 |

| Structure | Name | Ref |
|---|---|-----|
|  | 1-(4'-(methacrylate-ethyl)aminocarbonyloxymethyl)phenyl-3-(((methacrylate-ethyl)aminocarbonyloxyethyl)-3-methyl-triaz(1)ene | AT4 |
|  | 1-(4'-methacrylatemethyl)phenyl-3,3-di(2''-methacryloylethyl)-triaz(1)ene | AT5 |
|  | 1-(4'-(methacrylate-ethyl)aminocarbonyloxymethyl)phenyl-3,3-di(((methacrylate-ethyl)aminocarbonyloxyethyl)-triaz(1)ene | AT6 |
|  | 1-(3'-methacrylate-ethyl carboxyphenyl)-3-di(2''-methacrylate-ethyl)triaz(1)ene | AT7 |
|  | 1,2-Bis[1-(3''-methacrylate-ethyl)carboxyphenyl]-3-methyl]triaz(1)ene-ethane | AT8 |

| Structure | Name | Ref |
|-----------|---|------|
| | 1-(3'-ethyl glycidyl ether carboxyphenyl)-3-(ethyl glycidyl ether)-3-methyl-triaz(1)ene | AT9 |
| | 1-(3'-ethyl glycidyl ether carboxy-6'-methylphenyl)-3-(ethyl glycidyl ether)-3-methyl-triaz(1)ene | AT10 |
| | 1-(4'-methyl glycidyl ether)-3-(ethyl glycidyl ether)-3-methyl-triaz(1)ene | AT11 |
| | 2-methacrylatemethyl-5-(3'-(2''methacrylate-ethyl)-3'-methyl)triaz(1)ene-thiophene | AT12 |
| | 1,5-bis[4'-(methacrylatemethyl)phenylazomethyl-phosphonate]-diethylene glycol | AAP1 |
| | 1,5-bis[4'-(methyl glycidyl ether)phenylazomethyl-phosphonate]-diethylene glycol | AAP2 |

| Structure | Name | Ref |
|-----------|--|-----|
| | 2-Methyl-acrylic acid 5-methoxy-4-[2-(2-methyl-acryloyloxy)-ethoxy]-2-nitro-benzyl ester | NT1 |
| | 2-Methyl-acrylic acid 1-(5-methoxy-4-[2-(2-methyl-acryloyloxy)-ethoxy]-2-nitro-phenyl)-ethyl ester | NT2 |
| | 2-Methyl-acrylic acid 4,5-bis-[2-(2-methyl-acryloyloxy)-ethoxy]-2-nitro-benzyl ester | NT3 |
| | 2-Methyl-acrylic acid 2-(5-methoxy-4-[2-[2-(2-methyl-acryloyloxy)-ethoxycarbonyloxy]-ethoxy]-2-nitro-benzyloxycarbonyloxy)-ethyl ester | NT4 |
| | 2-[2'-nitro-4',5'-di(oxymethyloxirane)]benz yloxymethyloxirane | NT5 |

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| Structure | Name | Ref |
|---|---|-----|
|  | (2-Methoxy-5-nitro-4-oxiranylmethoxymethylphenoxy)-acetic acid oxiranylmethyl ester | NT6 |

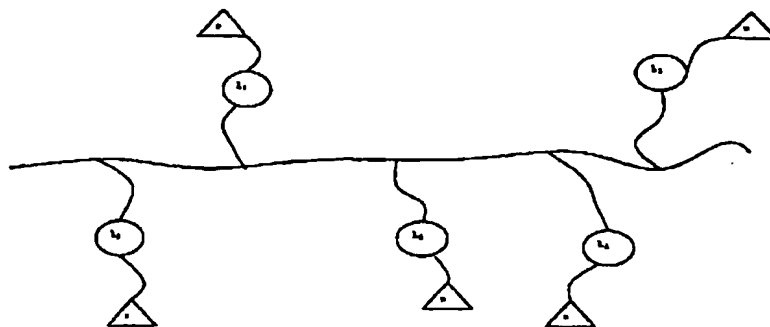
In a particularly advantageous variant of the invention, the bifunctional monomer is of oligomer or prepolymer size, optionally has more than two polymerizable units, and has a defined so-called "controlled" complex structure, i.e. the conditions and parameters of synthesis of these particular compounds enable the desired structure to be obtained.

The use of said bifunctional monomers in the adhesive composition of the invention offers advantages in respect of control over the viscosity of the composition and can reduce the well-known phenomenon of polymerization shrinkage and its disadvantages.

Two aspects are presented more particularly below which are found in the examples of bifunctional compounds and adhesive compositions of the invention.

A- According to a first aspect of this advantageous variant, the bifunctional monomer is a linear polymer having a branched comb structure in which the photocleavable units and the polymerizable units are preferably arranged on the comb branches of the principal linear chain of the polymer. Said bifunctional monomer may schematically be described as follows:

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where λ_2 is a photocleavable unit chosen from among the above-described photocleavable units or any other photocleavable unit photosensitive to a wavelength of λ_2 and $\triangle P$ is a polymerizable unit chosen from those described above.

In a first preferred alternative, the principal linear polymer chain is a chain whose structure may be chosen from among a large variety of possible structures, such as poly(ether), poly(ester), poly(acrylate), poly(amide), poly(acrylamide), poly(imide), poly(styrene), poly(urethane), poly(carbonate), poly(siloxane), poly(epoxide), poly-(phtalamide), poly(ethersulfonate), poly(alcene), poly-(aryltriazene), poly(arylasophosphonate), poly(o-nitrobenzyl) and any other conventional skeleton in polymerization techniques that is compatible with optional structural modification to allow grafting of the chain or the substituents contained in the chemical skeletons to link at least one photocleavable unit to at least one polymerizable unit, the bond between the photocleavable unit or units and the polymerizable unit or units being achieved in a way that conforms to definitions of bifunctional monomers of the invention, capable under radiation of wavelength λ_2 to photo-disrupt the principal branches of the linear chain of the polymer which therefore frees itself of the crosslinked polymer network obtained after polymerization of the adhesive composition.

In a second alternative, the branches comprising one or more photocleavable units and one or more polymerizable units may

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be synthesized in two or three steps, similarly to the general synthesis schema for bifunctional monomers set forth above, for example synthesis of the photocleavable unit directly on the pluri-substituted or poly-branched polymer chain followed by structural modification and/or followed by attachment of the polymerizable units, or grafting of the pre-synthesized photocleavable unit and attachment of the polymerizable units for example, or grafting of the "photocleavable unit-polymerizable unit" entity.

Advantageously, in a preferred embodiment of the two preceding alternatives, the principal linear chain can have substituents or can be modified so as to be provided with substituents able to set up a covalent bond with a chain whose chemical skeleton is made up of at least one photocleavable unit linked to at least one polymerizable unit, the achievement of this covalent bond being made using the synthesis modes described above for grafting vinyl polymerizable units.

A-a) In a particular embodiment, the branches have polymerizable functions of vinyl type at their ends.

One preferred manner to conduct grafting is "in one pot" synthesis in which the attachment of the vinyl unit is immediately followed by grafting of the "photocleavable unit(s)-vinyl unit(s)" branch, the two successive steps being based on the grafting reactions described previously for vinyl units. More precisely, the skeleton of the photocleavable unit terminates in two antagonist functions, for example one of these functions is typically -OR, -OCOR, NR_2 whilst the other function is essentially an acid or carboxylic ester.

The method for preparing said monomer consists of initially conducting the synthesis or grafting of a vinyl function through a nucleophilic substitution reaction on an acyl carbon. For an acid function, the reaction is preferably conducted in the presence of dehydrating agents such as 2-pyridinethiol, 1-methyl-2-chloropyridinium iodide, dicyclo-hexylcarbodiimide, N,N'-diisopropylcarbodiimide, N,N'-carbonyldiimidazole, 1,1'-carbonylbis(3-methylimidazolium) triflate, di-2-pyridyl

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carbonate, 1-hydroxybenzotriazole, an acylation agent of Pyridine/Tosyl Chloride type or SOCl_2 /DMF, preferably 1-methyl-2-chloropyridinium iodide, 2-pyridinethiol, dicyclohexylcarbodiimide, N,N'-diisopropyl-carbodiimide. For an ester function, the reaction is a transesterification that is preferably conducted in the presence of catalysts such as titanates, organic tin oxides and esters such as those cited above, using a basic catalysis method in the presence of non-ionic bases providing soft operating conditions such as amines (for example triethylamine, 1,2,2,6,6-pentamethyl-piperidine, 4-dimethyl-aminopyridine), amidines (e.g. 1,8-diazabicyclo[5.4.0]undec-7-ene), guanidines (e.g. 1,5,7-triazabicyclo[4.4.0]dec-5-ene, 1,1,3,3-tetramethyl-guanidine, 1,3-diphenylguanidine), triamino(imino)-phosphoranes; in preferred manner in the presence of guanidine derivatives, bisguanidines in particular as described in *Tetrahedron Letters* 39 (1998), 2743-2746), soluble polyguanidines or supported on a silica or polystyrene support described in *Reactive & Functional Polymers* 48 (2001), 65-74.

In a second step, the entity consisting of the photocleavable unit/vinyl unit obtained after the first step is grafted to a substituent of the principal linear polymer chain, said substituent ending in a function antagonist to an end function of the photocleavable unit/vinyl unit entity. The operating conditions are similar to those for the first step of the method.

A-b) In a further particular embodiment, the branches have polymerizable functions on their ends of vinyl or oxirane type.

A preferred method of grafting is three-step synthesis: the first step consists of grafting the skeleton of the photocleavable unit onto the substituents of the principal chain, the second is the structural modification of the grafted chemical skeleton (or graft), the third is the attachment of the polymerizable unit through creation or grafting. According to this embodiment, the grafting of the first step is the creation of a covalent bond using the same synthesis modes as set forth

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previously for the grafting of vinyl units. The structural modification of the second step is a conversion causing an "antagonist" function to appear on the end of the graft (such as previously designated F1 and F2) enabling the creation or grafting during the third step of polymerizable units according to the general synthesis modes described above for vinyl and oxirane units, or according to the more particular modes given under A-a) in the first particular embodiment of this first aspect of this advantageous variant of the invention.

The preferred conversions of the second step are the general reducing methods of carbon-heteroatom unsaturated derivatives (O or N) by carbon or heteroatom attack making it possible to create "antagonist" functions provided that they are compatible with the chemical skeletons (polymer chain, photocleavable unit, etc..). Reagents of choice are LiAlH_4 , NaBH_4 , AlH_3 , NaBH_4 for example in isopropanol, sodium triacetoxyborohydride, $\text{Li}(\text{Et}_3\text{CO})_3\text{AlH}$, ZnBH_4 in THF, or NaBH_4 in aqueous ethanol in the presence of CeCl_3 . Depending upon the type of polymer chain, aluminium isopropoxide in isopropanol is a method applicable to ketone reduction. The reagents derived from boranes such as BH_3 -THF, BH_3 -triethylamine, BH_3 - Me_2S , 9-BBN are generally adapted in most cases to the reduction of carbonyl compounds to obtain alcohol functions in the presence of photocleavable units such as aryltriazene or 2-nitrobenzyl.

The previously cited reagents, and more generally the derivatives of metallic hydrides, properly selected, may therefore be used to create alcohol or amine functions, from imine functions, Schiff bases, nitrile, epoxide, carboxylic acid derivatives with the exclusion of the nitro groups if a 2-nitrobenzyl function is present (therefore LiAlH_4 cannot be used in this instance).

Other conversions are possible for the second step:

- the generation of "antagonist" functions may also be made, depending upon the type of all the chemical skeletons present, using organometallic compounds added onto functions such as carbonyl, unsaturated α , β -carbonyl, imine, acid and derivatives,

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or oxirane. The preferred reagents are: Grignard reagents optionally in the presence of LiOCl_4 , $\text{Bu}_4\text{N}^+\text{Br}^-$, toluene, benzene, CeCl_3 , TiCl_4 , $(\text{RO})_3\text{TiCl}$, $(\text{RO})_3\text{ZrCl}$, $(\text{R}_2\text{N})\text{TiX}$, in particular when special functions are present; alkyl- or aryllithiums, 5 alkylzincs, tin allyltrialkyls, in the presence of BF_3 , Et_2O , allyltrialkylsilanes in the presence of a Lewis acid, allyl boranes; the conditions of the Reformatsky reaction (ketone or aldehyde, α -halo ester) in the presence of zinc.

• hydroboration of olefins is a particularly preferred 10 conversion, preferably on the ends of the skeletons of the photosensitive grafts, which enables soft generation of alcohol functions after hydrolysis in the presence of NaOH and hydroperoxide. Suitable reagents are BH_3 -THF, BH_3 -Me₂S or NaBH_4 combined with BF_3 , Et_2O , 9-BBN, mono/dialkylboranes.

• one applicable conversion depending upon the type of 15 chemical skeletons, is hydrolysis of imines, Schiff bases or isocyanates, optionally with acid or basic catalysis, to generate an amine function at the end of the photocleavable grafts.

• one particularly preferred conversion to obtain a primary 20 or secondary amine function consists of converting a halide derivative of 2-nitrobenzyl into aminomethyl-2-nitrobenzene for example by treatment with potassium phthalimide followed by hydrazinolysis, or into N-substituted aminomethyl-2-nitrobenzene by substitution in the presence of the corresponding N- 25 substituted amine.

Examples of such bifunctional prepolymer compounds, of polysubstituted linear polymer type, are:

- Poly((14-(2'-aminoacylethyl)-6-(hydroxymethyl)-1,4,8,11-tetraoxa-12-oxo-13-aza-tetradecane)-co-(7-(2'4'-aminoacylethyl)-1,4-dioxa-5-oxo-6-aza-heptane)), 30
- Poly[(14-(4'-aminoacylethexyl)-6-(hydroxymethyl)-1,4,8,11-tetraoxa-12-oxo-13-aza-tetradecane)-co-(7-(4'-aminoacylhexyl)-1,4-dioxa-5-oxo-6-aza-heptane)],
- Poly[(14-(4'-'(4''-aminocylphenyl)methylphenyl)-6-(hydroxymethyl)-1,4,8,11-tetraoxa-12-oxo-13-aza-tetradecane)-co- 35

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(7-(4'-(4''-aminoacylphenyl)methylphenyl)-1,4-dioxa-5-oxo-6-aza-heptane)],

- Poly[(14-(4'-(4''-aminoacylcyclohexyl)methylcyclohexyl)-6-(hydroxymethyl)-1,4,8,11-tetraoxa-12-oxo-13-aza-tetradecane)-co-
5 (7-(4'-(4''-aminoacylcyclohexyl)methylcyclohexyl)-1,4-dioxa-5-oxo-6aza-heptane)]

in which all these polymers are esterified on the hydroxy group at position 6 of the copolymer chain by groups of type:

- -oxycarbonyl-3-[3'-(2''-(methacrylate)ethyl)]-3'-methyl-
10 triazene) phenyl
- oxycarbonyl-ethyloxy-(1-methoxy-3-(methacrylatemethyl)-4-nitro)phenyl.

Preferred compounds of polysubstituted linear polymer type are:

- 15 • Poly[(14-(4'-methylaminoacylcyclohexyl)-6-(hydroxymethyl)-1,4,8,11-tetraoxa-12-oxo-13-aza-tetradecane)-co-(7-(4'-methylaminoacylcyclohexyl)-1,4-dioxa-5-oxo-6-aza-heptane)],
- Poly[(14-(4'-aminoacylbutyl)-6-(hydroxymethyl)-1,4,8,11-tetraoxa-12-oxo-13-aza-tetradecane)-co-(7-(4'-aminoacylbutyl)-
20 1,4-dioxa-5-oxo-6-aza-heptane)],

both being esterified on the hydroxy group at position 6 of the copolymer chain by groups of type: -oxycarbonyl-3-[3'-(2''-(methacrylate)ethyl)]-3'-methyltriazene]phenyl or of type -
25 oxycarbonyl-ethyloxy-(1-methoxy-3-(methacrylatemethyl)-4-nitro)phenyl.

These four preferred associations will respectively be referred to as: PU1AT1, PU1NT1, PU2AT1 and PU2NT1.

B- According to a second aspect of the variant in which the bifunctional monomer is of oligomer of prepolymer size, the
30 bifunctional monomer is a hyperbranched polymer whose structure derives from step polymerization of a type AB_n monomer, and is preferably derived from step polymerization of a monomer of type AB_3 or AB_2 , where A and B are respectively two different chemical functions capable of reacting together under condensation or

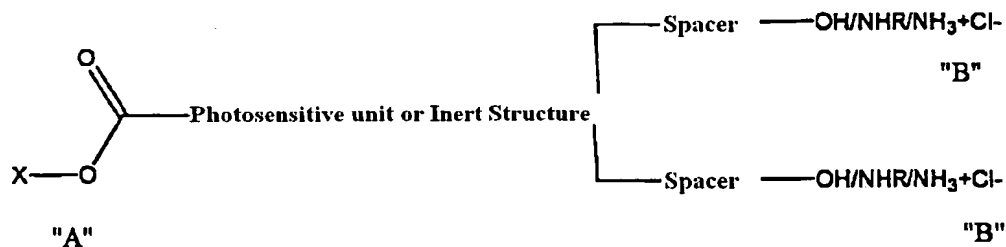
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addition reaction to give a polymer chain having branch point where every B function disappears.

In a first alternative, the hyperbranched polymer so designated has a "core" consisting in particular of monomer units having one or more photocleavable units in their skeletons and a "shell" around the core whose branches are formed of essentially inert monomer units from a photochemical viewpoint, the ends of the branches ending in at least one polymerizable unit, preferably only one.

In a second alternative, the hyperbranched polymer so designated has a "core" formed in particular of essentially inert monomer units from a photochemical viewpoint and a peripheral "shell" around the core whose branches consist of monomer units having one or more photocleavable units in their skeleton and whose branch ends terminate in at least one polymerizable unit, preferably only one.

The preferred general structure of a type AB₂ monomer able to polymerize following a step polymerization mode to give a hyperbranched polymer such as designated is as follows:



The functions A and B meet the criterion of antagonist functions and, in this respect, may be chosen from among all those previously described. In preferred manner, A is a function derived from carboxylic acid, preferably a carboxylic acid, carboxylic ester, carboxylate, trimethylsilylated carboxylic acid, acyl chloride function, and B is an alcohol function, optionally trimethylsilylated, esterified, a NH₂ amino group or a primary amine or primary ammonium salt. The preferred

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combinations are those in which A is a carboxylic acid function or ester and in which B is an alcohol or amino function.

Typical examples of AB₂ monomers are for example 2,2-bis(hydroxymethyl)propionic acid (inert monomer) and 1-(3'-carboxyphenyl)-3,3-di(2''-hydroxyethyl)triazene (photosensitive monomer).

The privileged preparation modes for these hyper-branched structures are based on the use of dehydrating agents, in particular if A is a carboxylic acid function, such as in particular 1-methyl-2-chloropyridinium chloride, dicyclohexylcarbodiimide, N,N'-diisopropylcarbodiimide, N,N'-carbonyldiimidazole, 1,1-carbonylbis(3-methyl-imidazolium) triflate, di-2-pyridyl carbonate, 1-hydroxybenzotriazole, an acylation agent of Pyridine/Tosyl Chloride type or SOCl₂/DMF, preferably 1-methyl-2-chloropyridinium chloride, 2-pyridinethiol, dicyclohexylcarbodiimide, N,N'-diisopropylcarbodiimide. If A is an ester function, the reaction is a transesterification preferably conducted in the presence of catalysts such as titanates, organic tin oxides and esters (in particular those already cited), using a basic catalysis mode in the presence of non-ionic bases providing soft operating conditions such as amines (for example triethylamine, 1,2,2,6,6-pentamethylpiperidine, 4-dimethylaminopyridine), amidines (for example 1,8-diazabicyclo[5.4.0]undec-7-ene), guanidines (for example 1,5,7-triazabicyclo[4.4.0]dec-5-ene, 1,1,3,3-tetramethylguanidine, 1,3-diphenylguanidine), triamino(imino) phosphoranes; in preferred manner, in the presence of the guanidine derivatives, bisguanidines in particular such as described in *Tetrahedron Letters* 39 (1998), 2743-2746, and polyguanidines either soluble or supported on a silica or polystyrene support as described in *Reactive & Functional Polymers* 48 (2001), 65-74.

Particular mention is made of the case in which the photocleavable units used are exclusively benzyl derivatives and more specifically 2-nitrobenzyl derivatives. In this case, the step polymerization reactions, in particular the

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polyesterification reactions, are advantageously conducted under conditions of acid catalysis (in the presence of sulfonic para-toluene acid or sulfuric acid for example), in addition to the preceding conditions which also apply.

5 As indicated at the beginning of this part concerning the privileged variant of bifunctional monomers, the structures are preferably controlled which means that for this second aspect a distinction is made between the preparation of the core and of the peripheral shell. In particular when the "core" is a
10 photocleavable core, the preparation methods are based on step polymerization methods by slow addition of the AB₂ monomers to a system of "core molecules" present in strong concentration in the reaction medium at all times relative to the concentration of reactive AB₂ monomers. These preparation methods, or derivative
15 methods, are described in particular in *Macromolecules*, 1998, 31, 3790-3801; *Macromolecules*, 2001, 34, 7692-7698; *Macromolecules*, 2002, 33, 3212-3218; *Macromolecules*, 2000, 33, 3099-3104; *Polymers for Advanced Technologies*, 2001, 12, 346-354. Advantageously the core is typically a photocleavable molecule of
20 B_n type and includes functions such as aryltriazenes or 2-nitrobenzyls, or is a hyperbranched polymer chain such as the one obtained by polycondensation of 1-(4'-carboxyphenyl)-3,3-di(2''-hydroxy-ethyl)triazene, of 1-(3'-carboxyphenyl)-3,3-di(2''-hydroxyethyl)triazene, or of 1-(3'-carboxy-6'-methylphenyl)-3,3-
25 di-(2''-hydroxyethyl)triazene in the presence of N,N-diisopropylcarbodiimide and APTS.

The preferred preparation methods use the attachment of polymerizable units to branch ends to give the bifunctional monomer of the invention, according to a final step in which the
30 polymerizable unit is created or it is grafted by attachment of a final photosensitive or inert layer of type AB_n monomers, which already carry polymerizable units. This final step is performed using all the possibilities indicated previously for the synthesis process according to the compatibilities offered by the
35 chemical structure of the synthesized polymers, in which preference is given to:

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- for vinyl units: possibilities 1°)1) to 1°)4) for creation, all of 2°) for grafting;

- for oxirane units: the first three manners for creation and the first and third manner for grafting.

5 For the first alternative of bifunctional structures of hyperbranched polymer type, namely with photosensitive core and inert shell, the following particular examples are chosen:

- Poly(1-(3'-carboxyphenyl)-3-,3-di(2''-hydroxyethyl)triazene),
- 10 • Poly(1-(3'-carboxy-6'-methylphenyl)-3-,3-di(2''-hydroxyethyl) triazene),
- Poly(1-(4'-carboxyphenyl)-3-,3-di(2''-hydroxyethyl)triazene),
- Poly(1-(3',5'-dicarboxyphenyl)-3-(2''-hydroxyethyl)-3-methyl-
- 15 triazene),

ω-functionalized by methacrylate ends with methacrylic acid and its derivatives, such as 2-hydroxyethylmethacrylate, glycidyl methacrylate or 2-isocyanatoethyl methacrylate for example, or by oxirane ends of glycidyl type by reaction with an

20 epihalohydrine, for example.

- Poly(1-(3'carboxyphenyl)-3-,3-di(2''-hydroxyethyl)triazene), ω-functionalized by the derivatives of methacrylic acid and which will be denoted PH1AT1.
- Poly(1-(3'-carboxy-6'-methylphenyl)-3-,3-di(2''-
- 25 hydroxyethyl)triazene), ω-functionalized by the derivatives of methacrylic acid which shall be denoted PH1AT2.

The above examples of hyperbranched structures are among the most simple which may be considered, the inert shell consisting of polymerizable units.

30 Other examples of hyperbranched structures with photosensitive core and inert shell are in particular:

- Poly(1-(3'carboxyphenyl)-3-,3-di(2''-hydroxyethyl)triazene-co-2,2-bis(hydroxymethyl)propionic acid),
- Poly(1-(3'-carboxy-6'-methylphenyl)-3-,3-di(2''-hydroxy-
- 35 ethyl)triazene-co-2,2-bis(hydroxymethyl)propionic acid),

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- Poly(1-(4'-carboxyphenyl)-3-,3-di(2''-hydroxyethyl)triazene-co-2,2-bis(hydroxymethyl) propionic acid),
 ω -functionalized by methacrylate ends with methacrylic acid and its derivatives, such as 2-hydroxyethylmethacrylate, glycidyl methacrylate or 2-isocyanatoethyl methacrylate for example, or by oxirane ends of glycidyl type by reaction with an epihalohydrine, for example
- Poly(1-(3'-carboxyphenyl)-3-,3-di(2''-hydroxyethyl)triazene-co-2,2-bis(hydroxymethyl) propionic acid),
 ω -functionalized by the derivatives of methacrylic acid and denoted PH2AT1;
- Poly(2,5-Bis-chloromethyl-1,3-dinitro-benzene-co-2,2-bis(hydroxymethyl)propionic acid) ω -functionalized by the derivatives of methacrylic acid and denoted PH2NT3.
- 15 • Poly((2-Nitro-4,5-bis-oxiranylmethoxy-phenyl)-methanol-co-2,2-bis(hydroxymethyl)propionic acid) ω -functionalized by the derivatives of methacrylic acid, and denoted PH2NT1.

For the second alternative of bifunctional structures of hyperbranched polymer type, namely with inert core and photosensitive shell, particular choice is made of:

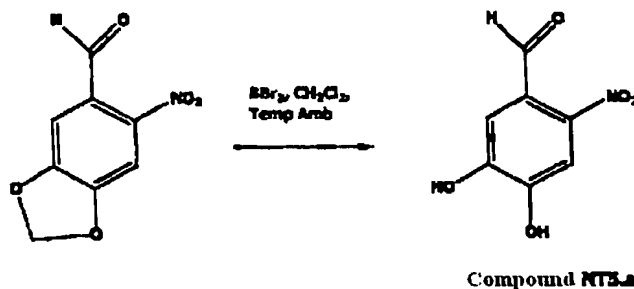
- Poly(2,2-bis(hydroxymethyl)propionic acid -co-1-(3'-carboxyphenyl)-3-,3-di(2''-hydroxyethyl)triazene),
- Poly(2,2-bis(hydroxymethyl)propionic acid -co-1-(3'-carboxy-6'-methyphenyl)-3-,3-di(2''-hydroxyethyl)triazene),
 ω -functionalized by methacrylate ends with methacrylic acid and its derivatives, such as 2-hydroxyethylmethacrylate, glycidyl methacrylate or 2-isocyanatoethyl methacrylate for example, or by oxirane ends of glycidyl type by reaction with an epihalohydrine, for example.
- Poly(2,2-bis(hydroxymethyl)propionic acid), ω -functionalized by an oxycarbonyl-3-[3'-(2''-(methacrylate)ethyl))triazene] phenyl group or an -oxycarbonyl-ethyloxy-(1-methoxy-3-(methacrylatemethyl)-4-nitro)phenyl group.

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DETAILED EXAMPLES OF BIFUNCTIONAL COMPOUND SYNTHESIS

Below is a detailed description of four examples implementing the method of fabricating bifunctional monomers of the invention, such as described previously in more general manner. On the basis of these examples of synthesis and proposed techniques, those skilled in the art will be able to obtain any photocleavable, polymerizable bifunctional monomer meeting the minimum required structural criteria for producing the photosensitive adhesive composition of the invention.

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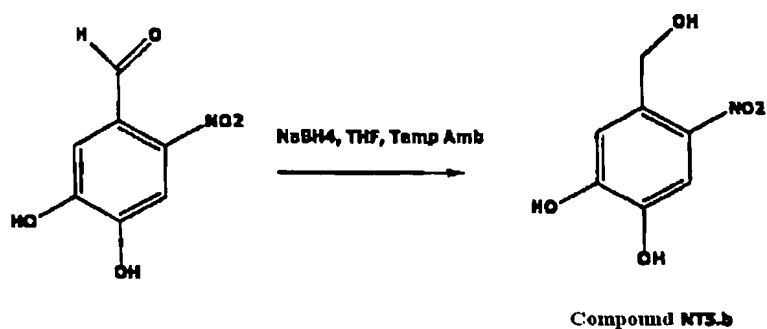
1. SYNTHESIS OF THE NT5 BIFUNCTIONAL MONOMERStep 1:

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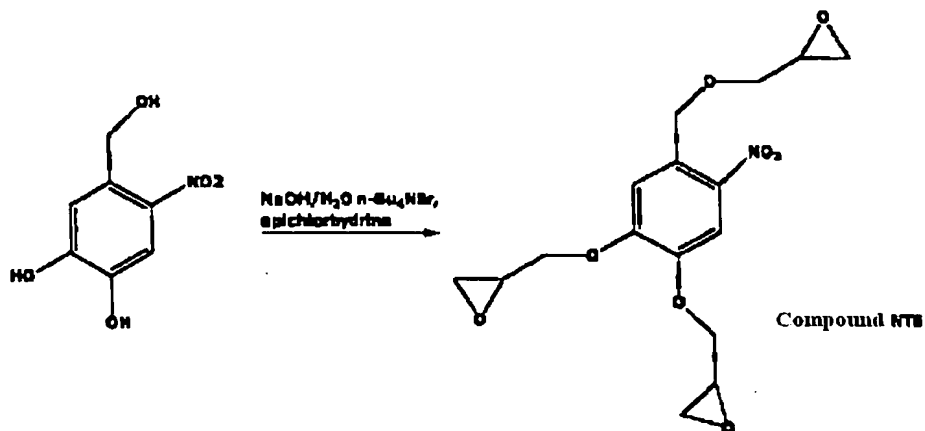
To a single neck, oven-dried, 100mL round-bottomed flask, are added 2g 6-nitropiperonal, then under inert atmosphere at 0°C, 30 mL BBr₃ (1.0M in CH₂Cl₂). The medium is then stirred at ambient temperature. 10mL BBr₃ (1.0M) are further added after 12h and 5mL after 24h. After 48h, the reaction medium is decanted into a 1 litre bottle placed over an ice bath and 100mL water are added very slowly. The mixture is concentrated. The residue is then collected with minimum volume THF and again cold precipitated by adding 35% hydrochloric acid. The precipitate is filtered through a glass sinter filter and the operation is repeated at least 3 times. The precipitated product is finally purified by flash chromatography on silica gel with an eluant (70mL/30mL/5mL petroleum ether/ethyl acetate/ethanol). 1.28 g of compound NT5.a are obtained.

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Step 2:

5 To a three neck, oven-dried round-bottomed flask, 1 g of
 NT5.a compound are added and 516 mg NaBH_4 . The flask is
 surmounted by a refrigerant and the assembly closed and placed in
 an inert atmosphere. Using a syringe, 100mL anhydrous THF are
 added. The reaction medium is stirred for 30h at ambient
 10 temperature. At the end of the reaction, 20 mL ethanol are added
 and left under stirring for 30 minutes. The reaction medium is
 concentrated, collected several times in THF and filtered. The
 grouped filtrates are concentrated and the residue is purified by
 flash chromatography on silica gel with eluant (70mL/30mL/10mL
 15 petroleum ether/ethyl acetate/ethanol). 960 mg of compound NT5.b
 are obtained.

Step 3:

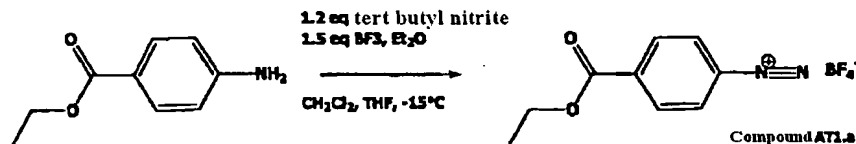
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To a 200mL three neck round-bottomed flask, 16mL aqueous solution containing 50 % potassium hydroxide and 11ml epichlorohydrine are added together with 380 mg tetrabutyl-ammonium bromide. The mixture is stirred at 0°C and followed by cold, progressive addition of 1.5 g NT5.b so that the temperature does not exceed 25°C. After a reaction time of 15h, the medium is poured into 30mL of a water/ice mixture. The aqueous phase is extracted with ethyl ether (3*60mL). The organic phases are grouped together and washed with an aqueous solution of NaCl (5*60mL), dried on sodium sulfate and concentrated. The residue is distilled under reduced pressure and purified by flash chromatography on silica gel with an eluant (90mL/10mL petroleum ether/ethyl acetate) to yield 1.26g of compound NT5.

II. SYNTHESIS OF THE AT1 BIFUNCTIONAL MONOMER

Step 1:

- a) The diazonium tetrafluoroborate salt of 4-ethyl-aminobenzoate was prepared (hereafter denoted AT1.a):



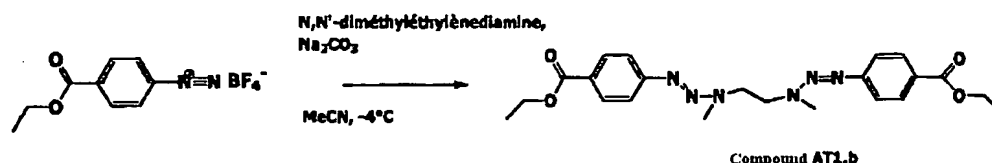
To a three neck, oven-dried round-bottomed flask, 15g ethyl 4-aminobenzoate are added in 300 mL dry CH₂Cl₂ and 50mL dry THF. The medium is placed in an inert atmosphere and the flask is immersed in a bath cooled to -15°C. 19.35g BF₃·Et₂O are then slowly added in 40mL dry CH₂Cl₂. When thermal equilibrium is reached 12.5g tert-butyl nitrite is added over 1h30 in 80 mL dry CH₂Cl₂ and the medium is maintained under vigorous stirring. When addition is completed, the medium temperature rises to 0°C. Approximately 150 mL pentane are then added to the reaction medium. The formed precipitate is filtered, then washed with 300mL ethyl ether, filtered again and finally dried at 25°C in a

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drying oven in the presence of P_2O_5 . 23.1g of compound AT1.a are obtained.

b) Diazoic coupling was performed and a compound hereafter designated AT1.b is obtained:

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In 250mL dry MeCN, 15.4g AT1.a is dissolved and 12.82g sodium carbonate is added. The medium is cooled in an inert atmosphere over a bath at $-4^{\circ}C$. 4.4g N,N'-dimethylethylenediamine are added to an addition funnel in 160mL dry MeCN in the presence of sodium carbonate. The addition to the reaction medium is conducted over 6h under vigorous stirring. When addition is completed, stirring is maintained for 1h30. The reaction medium is then filtered and the salt is washed in ethyl acetate. The product is isolated by successive dissolutions of the crude residue in a minimum volume of ethyl ether, cold crystallization and filtration of the precipitate. The product is dried in a drying oven in the presence of P_2O_5 and 12.03g of the compound AT1.b are obtained.

Step 2:



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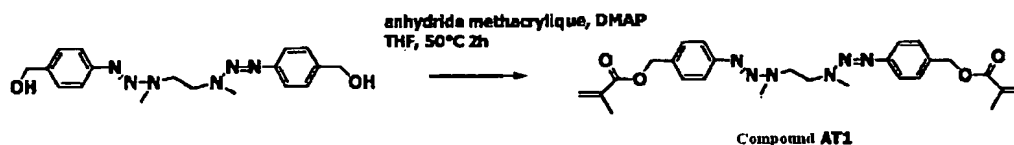
One half-spoon $LiAlH_4$ is placed in a three neck round-bottomed flask, previously oven-dried and fitted with a refrigerant and an addition funnel,. The assembly is placed in an inert atmosphere and immersed in an oil bath at $55^{\circ}C$. 4g AT1.b compound dried on P_2O_5 are previously placed in the addition

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funnel. 40mL dry THF are then added to the flask and 100mL to the addition funnel. The AT1.b compound is then added drop by drop to the flask under vigorous stirring, and gradually, 120mL dry THF and 1.8g LiAlH_4 , divided into several fractions are directly added to the reaction medium. The medium is stirred at 50°C for 3h. At the end of the reaction, a mixture of 50mL THF and 50mL ethyl acetate is added slowly, the crude is passed through the glass sinter and the collected solid is washed in methanol until it becomes white. The filtrates are concentrated, washed in a mixture of methanol and THF, and the recrystallized solid is filtered through a sinter. These operations are repeated until practically all the aluminates have been drawn from the AT1.c compound of which 3.23g is obtained.

15

Step 3:

20

To an oven-dried three neck round-bottomed flask surmounted by a refrigerant, are added 1.219g AT1.c compound dried on P_2O_5 and 2.5g 4-dimethylaminopyridine (DMAP). The medium is placed in an inert atmosphere and brought to 50°C. Using a dropping funnel, 150mL dry THF are added to the reaction medium under stirring. After 5 minutes, a syringe is used firstly to add 1.55mL methacrylic anhydride with +0.3 weight % hydroquinone, then 50mL dry THF in the dropping funnel. The additions are made slowly to the mixture for one hour and the temperature is then maintained at 50°C for a further hour, then stirring is continued for 12h at 20°C.

30

The reaction medium is then extracted with THF and is cold concentrated. The residue is then extracted by a succession of

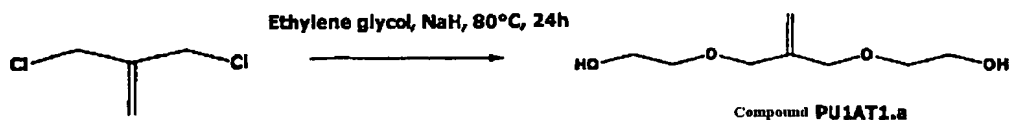
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biphase separations. The crude is first dissolved in 125mL CH_2Cl_2 . This first phase is extracted with 150mL iced water, which is in turn extracted with 50mL CH_2Cl_2 .

The operation is repeated three times. After grouping the organic phases together and drying on sodium sulfate, they are evaporated and the residue is purified by flash chromatography on silica column with an eluant (85mL/4mL/13mL petroelum ether/ethyl ether/ethyl acetate). 1.53g of compound AT1 are obtained.

10 III. SYNTHESIS OF THE PU1AT1 BIFUNCTIONAL MONOMER

Step 1:

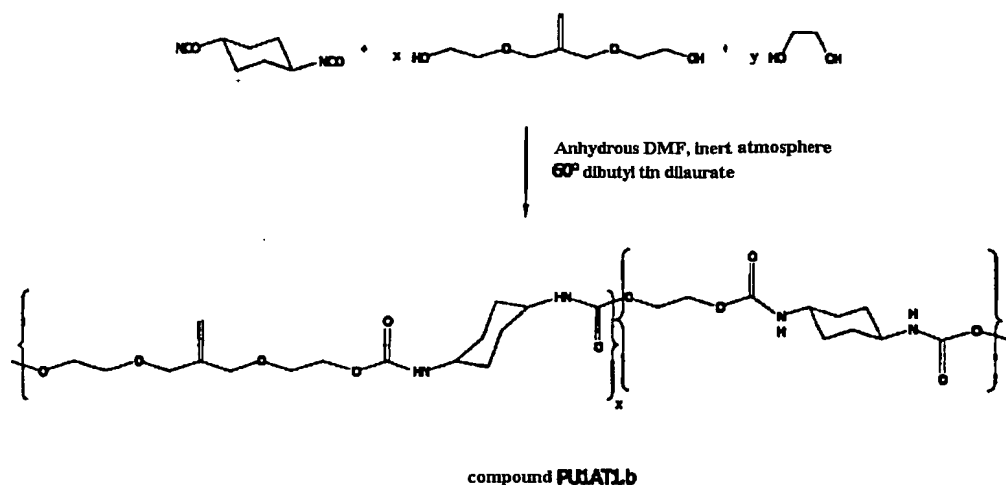


15 To an oven-dried, three-neck round-bottomed flask fitted with a magnetic stirrer and surmounted by a refrigerant, 450mL distilled anhydrous glycol ethylene are added under an inert atmosphere. 14mL 3-chloro-2-chloromethyl-1-propene are added using a syringe. The flask is immersed in an oil bath at 60°C, under vigorous stirring. 12g 95%NaH are prepared in several
20 portions and the entire quantity of NaH is carefully added in small successive portions to the reaction medium. When addition is completed, the bath temperature is set at 80°C and it is left under stirring for 24h.

25 At the end of the reaction, the mixture is distilled under reduced pressure of 4mm Hg at a temperature of 80°C to 140°C so as to remove a maximum amount of ethylene glycol. The residue is purified by flash chromatography on silica gel with eluant (85mL/15mL/2-10mL petroleum ether/ethyl acetate /ethanol). The
30 product is again concentrated by distillation under reduced pressure and 16.8g of compound PU1AT1 is obtained with 57.8 weight percentage in a mixture with residual ethylene glycol.

Step 2:

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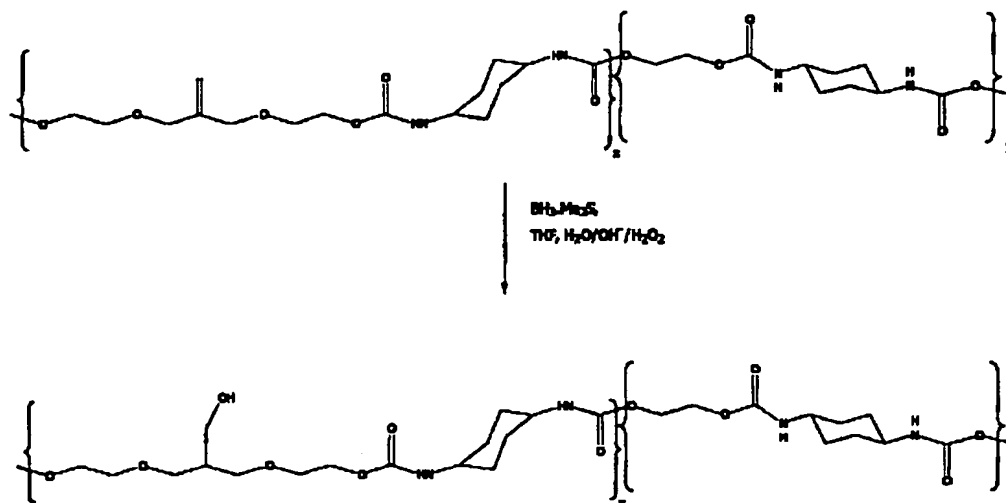


In an oven-dried, single neck round-bottomed flask, a magnetic stirrer is placed with 3.555g of a previously obtained and freshly distilled PU1AT1.a/ethylene glycol mixture. After desolvation under reduced pressure of 4mmHg for 15h, the medium is placed in an inert atmosphere. Using a syringe, 5.397g 1,3-bis(isocyanatomethyl)-cyclohexane are added thereto. 2mL anhydrous DMF and 8 drops of dibutyl tin dilaurate are then added. The flask is immersed in an oil bath at 65°C and left under stirring for 72h. At the end of the reaction, all the DMF is vacuum distilled at 40°C and a weight of approximately 8.9g of compound PU1AT1.b is recovered.

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Step 3:

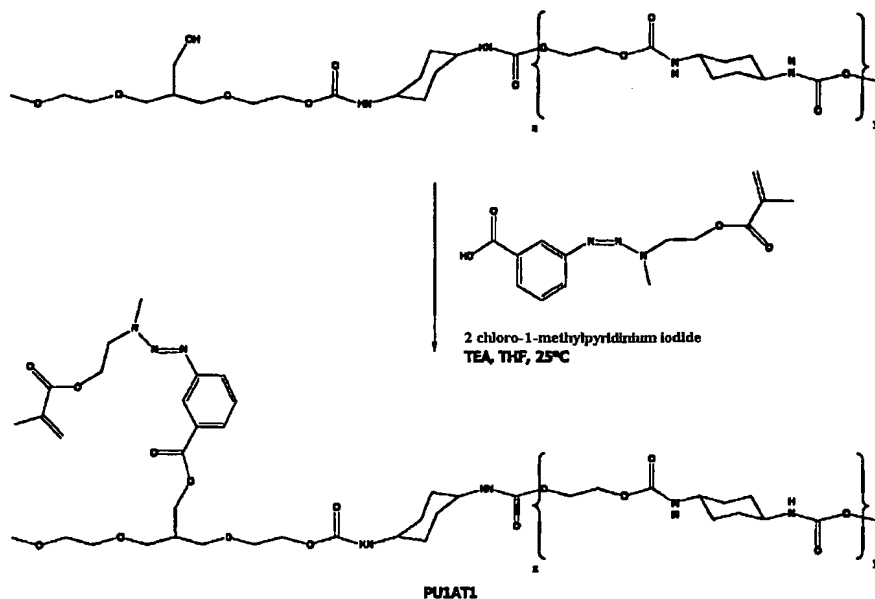
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Compound **PU1AT1.c**

To a twin neck oven-dried round-bottomed flask, 0.516g PU1AT1.b polymer are placed with a magnetic stirrer. The flask is placed in a vacuum overnight. The flask is then placed under a stream of nitrogen and 20mL anhydrous THF are added. The flask is immersed in an ice bath and 0.2mL $\text{BH}_3 \cdot \text{Me}_2\text{S}$ are added. Stirring is maintained for 2h30, then successive cold additions are made of 0.1mL distilled water, 0.1mL 3M NaOH, 0.5mL THF, 0.17mL absolute ethanol and 0.18mL 30% H_2O_2 . The mixture is brought to 40°C for 3 hours under vigorous stirring. At the end of the reaction, it is concentrated then 70mL CH_2Cl_2 are added to the residue and the precipitate is filtered. The collected filtrate is concentrated, washed and extracted with CH_2Cl_2 several times. Further concentration is performed and 5mL methanol with 40mL ethyl ether are added, followed by filtration and concentration. 415mg of the compound PU1AT1.c are obtained.

Step 4:

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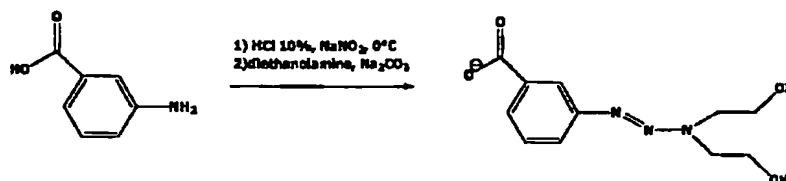


To a dried, three neck round-bottomed flask, 0.980g of 2-chloro-1-methylpyridinium iodide are added. The flask is fitted with a dropping funnel containing 500mg dried PU1AT1.C, and with a second dried single neck round-bottomed flask containing 350mg 1-(3'carboxyphenyl)-3-(2''-hydroxyethyl)-3-methyltriaz(1)ene and connected via tubing to the three-neck flask. The assembly is placed under nitrogen, 60ml anhydrous THF are added to the reaction medium with 134mg methacrylic acid and 165mg distilled triethylamine. Stirring is carried out for 15 minutes then the content of the second flask is added by pouring. Stirring is conducted for 3 hours and then 5g triethylamine and 20 mL anhydrous THF are again added to the addition funnel. The dissolved PU1AT1.c polymer is then added to the reaction medium and it is left under stirring for 24h at ambient temperature. At the end of the reaction, the reaction medium is concentrated and filtered. The precipitate is washed in ethyl ether and the filtrate is concentrated. The obtained crude is dissolved in 40mL dichloromethane and the organic phase is washed with 10 times 50mL water at pH 5-6. The organic phases are dried on sodium sulfate and concentrated. The residue is washed several times in pentane and 415mg PU1AT1 is obtained.

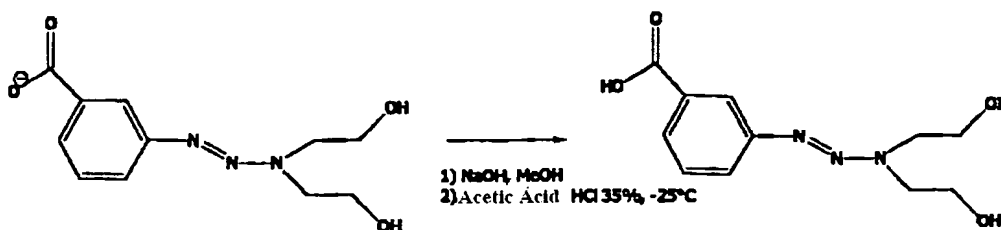
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IV. SYNTHESIS OF THE PH2AT1 BIFUNCTIONAL MONOMER

Step 1: Synthesis of the precursor 1-(3'-carboxyphenyl)-3,3-di(2''-hydroxyethyl)triazene PH2AT1.a.



6.857g 3-aminobenzoic acid are dissolved in a mixture of
 10 16mL concentrated hydrochloric acid (35%) and 35mL water cooled
 by an ice bath in a twin neck round-bottomed flask. The flask is
 fitted with an addition funnel in which an aqueous solution of
 sodium nitrite has been placed (3.45g in 40mL) to which is added
 drop by drop the solution of aminobenzoic acid while controlling
 15 the temperature of the solution which must remain below +2°C.
 After addition, stirring is maintained for 30 minutes. The
 solution obtained is collected and stored at 0°C. In another twin
 neck round-bottomed flask, another aqueous solution of
 diethanolamine (10.5g) is prepared saturated with sodium
 20 carbonate. This solution is cooled by an ice bath. Under vigorous
 stirring, the diazonium salt solution, to which crushed ice is
 regularly added, is added drop by drop for 45 minutes and
 stirring is maintained for a further 1h30. After coupling,
 concentration is conducted in a rotary evaporator to recover the
 25 carboxylate.



Compound PH2AT1.a

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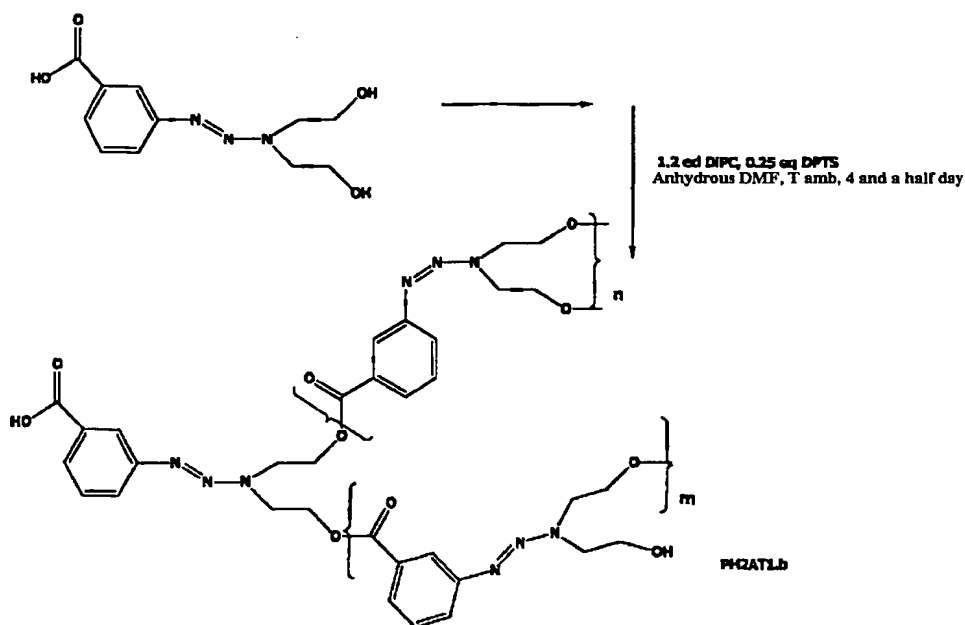
The excess sodium carbonate is removed by distillation of the solid in a minimum volume of acetonitrile and filtration. The filtered solution is concentrated. The sodium carboxylate salt is washed through the addition of 75mL methanol and 3mL 35% NaOH aqueous solution. The solution obtained is stirred for one hour at ambient temperature and then concentrated. Finally 45mL water are added then, under thermal equilibrium with an ethanol bath at -30°C and stirring, 6.8mL of a solution containing 3mL acetic acid and 17mL water is added. Under constant stirring a sufficient number of drops of 35% concentrated hydrochloric acid are added gradually until a true precipitate is obtained in a solution whose pH must be reduced to 4-5. Under these conditions, 150mL of very cold water are added and filtration is immediately performed through a glass sinter. After washing in cold water until filtrates are neutral and removing a maximum amount of water, the precipitate is placed in a vacuum oven at 30°C for a whole day and 8.92g of PH2AT1.a product are obtained.

20 Step 2: Polycondensation of 1-(3'carboxyphenyl)-3,3-di(2''-hydroxyethyl)triazene to obtain PH2AT1.b

To an oven-dried, three-neck round-bottomed flask, passed in a Bunsen burner flame alternately under a vacuum and a stream of nitrogen, are added 0.5g dry PH2AT1.a and 0.124g dry DPTS (4-(N,N-dimethyl-aminopyridinium)tosylate).

Using a syringe, 3mL anhydrous DMF are then added. Under stirring, 0.45mL N,N-diisopropylcarbodiimide are added with a syringe over a total time of 4 and a half days.

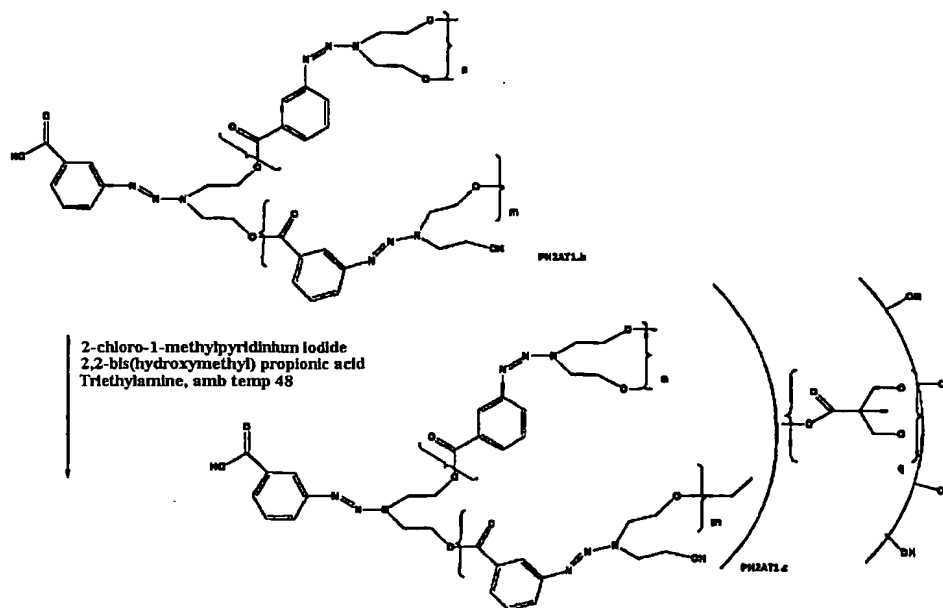
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At the end of the reaction, the urea precipitate is filtered through a glass sinter, then repeated precipitation of the polymer is caused by pouring the solution obtained in minimum volumes of a very cold (10% methanol/90%water) mixture and at least an equivalent volume of crushed ice. The filtrate obtained after filtering through a glass sinter is systematically extracted following an identical protocol after concentration in a rotary evaporator. On completion, 0.164g of a dark brown solid of the PH2AT1.B polymer were recovered after a 2-day residence time in a vacuum oven at a temperature of 35°C.

Step 3: Synthesis of an inert shell of poly(2,2'-bis-hydroxymethylpropionic acid): Obtaining the PH2AT1.c polymer.

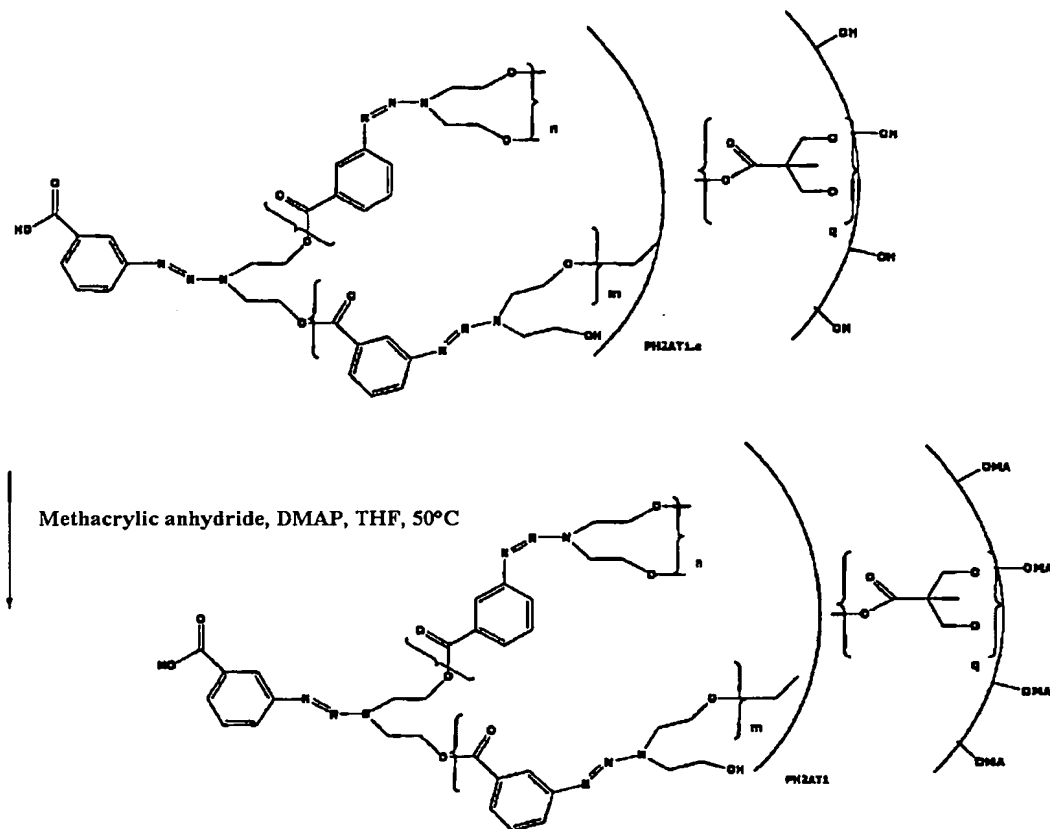
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To a three neck round-bottomed flask dried as in the preceding step, 0.3g PH2AT1.b are added together with 12.5g 2-chloro-1-methylpyridinium iodide. The flask is connected to a second, dried, single neck round-bottomed flask containing 5.5g oven-dried 2,2-bis (hydroxymethyl)propionic acid. The medium is placed in an inert atmosphere and immersed in a temperature-controlled bath at 30°C. Using a syringe, 100mL distilled triethylamine are added and 5 ml anhydrous DMF. Under constant stirring, in successive solid portions, the 2,2-bis(hydroxymethyl)propionic acid is added over a period of 48h. At the end of the reaction, the mixture is vacuum concentrated at 4mmHg and extracted several times with dichloromethane. A solid is collected through glass sinter and washed several times with aqueous solutions of pH 6-7 then again with dichloromethane and finally collected and placed in a vacuum oven for 2 days at 35°C. 3.4g PH2AR1.c are obtained.

Step 4: Methacrylic functionalization of PH2AT1.c to obtain PH2AT1:

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To an oven-dried three neck round-bottomed flask surmounted by a refrigerant and fitted with an addition funnel, 3,4g
 5 PH2AT1.c are added with 15.37g DMAP. The medium is brought to 50°C, placed under nitrogen and 500mL anhydrous THF are added using a syringe. To the addition funnel 13.75g (0.2 weight % hydroquinone) of methacrylic anhydride are added using a syringe. Finally, 100mL anhydrous THF are added to the addition funnel and
 10 the addition of methacrylic anhydride is started drop by drop for 4 hours under vigorous stirring. When addition is completed, the temperature is left to return to 25°C overnight. The reaction crude is concentrated in a rotary evaporator and dissolved in 300mL ethyl acetate. This phase is extracted several times with
 15 volumes of 300mL water at pH 5. The organic phases are grouped together, dried, concentrated and passed through R545 celite with dichloromethane. The organic phases are concentrated, re-

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dissolved in 300mL ethyl acetate and extracted with volumes of 300mL water at pH 5. After drying on magnesium sulfate, the organic phases are concentrated and 3.55g PH2AT1 are obtained.

5 According to an essential characteristic of the invention, the photosensitive adhesive composition contains initiation means whose constituents may be most varied in relation to applications and desired properties. Several variants of the initiation means can be considered, each one suited to the
10 polymerization process (radical, cationic or anionic) chosen by the formulator. In particular, the initiation means may be multiple and in this case the initiation system is a multicomponent initiation system which may give rise to hybrid or dual chain polymerization or crosslinking.

15 The examples given below do not limit the invention in any way and are intended to enable the formulator to make the best choice among available compounds, in particular in relation to desired use of the adhesive composition of the invention.

 In a first variant of initiator means, these are of
20 chemical type.

 For radical chain polymerization, examples are limited to the description of particular use in the area of dentistry or medical prostheses. Therefore said initiator means may consist of at least two compounds reacting together under a redox mechanism
25 to generate free radicals. A more particular example, routinely used in dental art, consists of mixing an electron acceptor such as benzoyl peroxide or dibenzoyl peroxide with an electron donor such as tertiary arylamine. Another possible example is the oxide of tri-n-butyl borane.

30 For cationic chain polymerization, the initiator of chemical type may be chosen from among:

- a) Brönsted acids such as perchloric acid, trifluoromethylsulfonic acid, trifluoroacetic acid, iodohydric acid,
- 35 b) Lewis acids, of which the most common are BF_3 , AlCl_3 , TiCl_4 , SnCl_4 , SbCl_5 , the Lewis acid optionally being associated

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with a weak acid or a cationising agent such as water, a carboxylic ester, a sulfonic ester, an ether or alkyl halide.

Finally, anionic initiation for an adhesive composition of the invention may be used in accordance with the type of polymerizable units chosen, with:

- Lewis bases such as benzylsodium, for example, phenylisopropylpotassium or the (n-,sec-, tert-) isomers of butyllithium.

- bases such as KOH or amines.

However, for the implementation of this polymerization process, persons skilled in the art may be led to taking some precautions, such as the addition of complexing agents, for example Et_2Zn to protect sensitive functional groups.

Also, anionic initiation of chemical type, for an adhesive composition of the invention, requires special conditions (highly anhydrous conditions, controlled atmosphere for example) which may limit their use to specific applications of the adhesive composition or require the preparation of a polymerized adhesive of the invention that is applied to the surfaces of the items to be bonded after polymerization time.

In addition, the adhesive composition of the invention, coming within the scope of the first variant of the initiator means, is most often in the form of "adhesive sub-compositions" optionally comprising additive solvents, which the formulator must mix before use and before coating the surfaces to be bonded to obtain a complete photosensitive adhesive composition of the invention able to provide required adhesiveness between the parts to be bonded and so as to avoid any premature polymerization of the adhesive composition or any long-term storage problem.

According to a second variant of the initiator means, these may consist of at least one photoinitiator able to initiate the polymerization mechanism under the action of crosslinking radiation whose wavelength λ_1 is preferably fairly different to that of uncrosslinking radiation λ_2 . In this disclosure, λ_1 and λ_2 designate both single wavelength radiation and ranges of wavelengths centered on the given values. Also, the expression

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"crosslinking radiation" denotes electromagnetic radiation capable of stimulating the generation of free radicals, cations or anions. The expression "uncrosslinking radiation" denotes electromagnetic radiation capable of causing the hardened adhesive to lose at least part of its integrity.

1- According to a first aspect of this variant of initiation means, these are photoinitiation means at wavelength λ_1 .

For the mechanism of radical chain polymerization, this first aspect has three versions:

a) In a first version of this aspect, the photoinitiator is of the type able to generate free radicals via a mechanism of homolytic photocleavage. The photoinitiators giving rise to such processes belong to various families and the photoinitiators of the invention may be chosen from the categories derived from the following known examples: benzyl dialkylcetal, benzoin ether, α -hydroxy, α -alkyl phenylketone, cyclohexanol benzoyl, oxides of trimethylbenzoyl phosphine and more generally bis-acyl-oxides of phosphine, α -amino thioalkylphenylketone, α -amino morpholino-phenylketone, sulfonic esters of α -hydroxy methylbenzoin. There also exist numerous other photocleavable initiators in which radical generation occurs subsequent to a series of consecutive homolytic cleaving processes. The chief examples known to persons skilled in the art are the esters of benzoyl oxime, arylarylsulfides, peroxides, peroxides containing a chromophore such as benzophenone or any alkylphenone, disulfides, ketosulfides and azoic compounds such as AIBN (azobisisobutyronitrile) or azobenzoines.

b) In a second version, the photoinitiator is of the type able to create free radicals through a mechanism of atom snatching. The most frequent class of these photoinitiators is in the one in which a proton is snatched from a substrate during photoreduction of a triplet $n\pi^*$ state of the photoinitiator, the main examples being the derivatives of benzophenone, of thioxanthenes, of benzyl, of 1,2-diketones such as camphorquinone, and ketocoumarins. Formulators have at their

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disposal other photosensitive compounds, onium salts such as the salts of triarylsulfonium in particular, the salts of alkylarylsulfonium and diarylhalonium salts, largely described in particular by J.V.Crivello. These compounds are generally given
5 wide used as photoinitiators for cationic polymerization (cf. appropriate paragraph below); however, the interaction of the triplet state with a proton donor produces free radicals also enabling initiation of a radical process.

c) The third version concerns the use of photoreducible
10 photoinitiators. The creation of free radicals is consecutive to electron transfer. The families of compounds behaving in this way are chromophors of diarylketone, camphorquinone, ketocoumarin type or aromatic dyes of xanthene, fluorone, thioxanthone, thiazine, acridine, anthraquinone, cyanine, merocyanine,
15 benzopyrane type. The family of photoreducible aromatic dyes is likely to be of especial interest to formulators of dental resins insofar as these photoreducible aromatic compounds are excitable in wavelengths of the visible range.

Regarding cationic chain polymerization, this first aspect
20 also comes in three versions:

a) the photoinitiator is of the type capable of generating a cationic species, more particularly a HX Brönsted acid under $\lambda 1$ radiation, by direct photodecomposition optionally in the presence of a proton donor, optionally by interacting with
25 polymerizable functions such as epoxide functions for example. The photoinitiators of the invention may be chosen from among the onium salts of diarylhalogenium, triarylsulfonium, dialkylarylsulfonium or dialkyl-phenacylsulfonium type. For example one of the following compounds may be chosen: bis[4-
30 (diphenylsulfonio)-phenyl)sulfide bishexafluorophosphate, triphenylsulfonium tetrafluoroborate, hexafluoroantimonate of (S-methyl-S-dodecyl-S-phenacyl)sulfonium, hexafluoroantimonate of (4-n-decyloxyphenyl)phenyl-iodonium, hexafluorophosphate and tetrakis(pentafluorophenyl)borate of 4-methylphenyl-4-(1-
35 methylethyl-)phenyliodonium.

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Conventionally, the counter-anions are chosen from among: BF_4^- , PF_6^- , AsF_6^- , SbF_6^- , RSO_3^- . With a view to increasing the sensitivity in the near UV or even the visible, structures may preferably be chosen such as 4-thiophenoxy triarylsulfonium or the alkylaryl derivatives (9-phenylthioanthracenyl)-10 sulfonium, the bisiodonium salts having for example covalent oxy, carbonyl, sulfonyl bridges between the diaryliodonium groups.

b) the photoinitiator is of the type capable of generating a Brönsted acid or Lewis acid under \square l radiation. The photoinitiators of the invention may be chosen from among the diazonium salts in the absence or presence of hydrogen donors.

c) the photoinitiator is of the type capable of generating a cationic species, more particularly a Brönsted acid, under the action of cleavage of a photoinduced covalent bond as is the case for example for derivatives of N-(trifluoromethoxysulfonyl)phtalimide or of 6,7-(trifluorosulfonyl)coumarin, the sulfonic esters of 2-nitrobenzyl derivatives, all generating $\text{CF}_3\text{SO}_3\text{H}$.

Finally for this first aspect of the photoinduced initiation variant, formulators may have recourse for anionic chain polymerization to the following compounds given as examples:

- halides of trimethylfluorenylammonium and trimethylbenzylammonium;
- base photogenerating o-nitrobenzyl derivatives, for example dimethyl 4-(o-nitrophenyl)-2,6-dimethyl-1,4-dihydro-3,5-pyridinedicarboxylate, derivatives of 2-nitrobenzyl-carbamates, bis(benzophenone oxime) N,N'-hexamethylene diurethane, N-alkylated nifedepine;
- O-acyloxime derivatives such as O-phenylacetyl-2-acetonaphthone;
- quaternary ammonium dithiocarbamates.

2- According to a second aspect of the photoinitiation variant, the initiation system may be a bi-component system (photoinitiator + co-initiator). Within the present invention,

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the description of this aspect is limited to radical chain polymerization in which the two components together produce electron transfer under radiation at wavelength λ_1 . This is only a particular case of the concept of bi-component photoinitiation.

5 One possibility is the combination of an electron acceptor photosensitive species and an electron donor species. This combination is generally the one that is most described it enables numerous associations to be considered. Hence, the electron acceptor photosensitive species include all the families
10 previously set forth in respect of photoreducible photoinitiators. Within this strategy, the electron donor species accelerates radical polymerization over a two-step process, namely electron transfer followed by proton transfer. Numerous species exist that are able to interact with photoreducible
15 species and compounds may be chiefly cited which include an activated nitrogen atom such as triethanolamine, a tertiary amine or a tertiary arylamine (N,N-dimethyl-p-toluidine, N,N-diethanol-p-toluidine, N,N-dimethyl-sym(m)xylylidine, 3,5-di-tert-butylaniline, N,N-dimethyl-p-ethyl aminobenzoate), the compounds
20 comprising an activated nitrogen and sulfur atom such as the thiazole derivatives (mercaptobenzothiazole), boron salts (borate) such as tetraphenylborates or butyltriphenylborates and other salts of tetraalkylammonium tetraorganylborate type.

Onium salts also hold an important place among bi-component
25 systems when associated with boron salts, such as the derivatives of tetraphenylborate and, more preferably, derivatives of butyltriphenylborate. On account of strong absorption below a wavelength of 300nm and a "tail" of the absorption spectrum in the visible beyond a wavelength of 400nm, even 430 nm in some
30 cases, these compounds are photosensitive both in the UV and in the visible range.

3- According to a third aspect of the photoinitiation variant, the initiation system is a a photoinitiation system comprising, in addition to the photoinitiator proper, at least
35 one species able to photosensitize the initiator means creating the active centres (free radicals, cations or anions); this

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species is called photosensitizer. In this case, the interaction between the photosensitizer in one of its excited states with the photoinitiator may principally, this description not being exhaustive, be of two types. Photosensitization operates either
5 by singlet state-singlet state or triplet state-triplet state energy transfer, or by electron transfer photoinduced with the photosensitizer, or else by both at the same time.

If at least one of the photoinitiators is of the type able to generate free radicals by homolytic photocleavage mechanism,
10 then a certain number of systems exist in the literature which enable this process to be accelerated. For example an important class of initiators is the peroxides, but the photosensitization mechanisms are most varied. For example, benzoyl peroxide, decanoyl peroxide may be photosensitized by energy transfer from
15 the triplet state of compounds such as anthracene, acetophenone, methoxy- and cyanobenzophenones, associated with the formation of a charge transfer complex. In other cases, electron transfer is involved as between a thioxanthene for example with 3,3',4,4'-tetra-(t-butylperoxycarbonyl)-1-benzophenone. These examples are
20 only given by way of indication, having regard to the variability of sensitization mechanisms in relation to operating conditions and the chemical species involved.

Other examples of importance concern the interaction which exists between an α -amino acetophenone (e.g. α -morpholino
25 thiomethylphenylketone) and a photosensitizer of thioxanthone type. This system has the particular feature of being able to function both by energy transfer from the triplet state of thioxanthone and by electron transfer.

It is also possible to photosensitize some bi-component
30 systems which associate an electron donor and acceptor. In particular, the onium salt, "intermediate" photoreducible sensitizer and electron donor trio is very efficient in initiating acrylic formulations. In particular the following combinations may be made between:

35 - an onium salt chosen from among the diaryliodonium salts and triarylsulfonium salts,

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- an intermediate photosensitive and photoreducible species chosen from among the categories designated by the following examples: di(aminoarylketone), ketocoumarin, thioxanthone, xanthene, fluorone, thiazine, acridine, anthraquinone, cyanine, merocyanine and benzopyrane, and

- an electron donor such as the compounds containing an activated nitrogen atom, for example a tertiary amine and a tertiary arylamine (N,N-dimethyl-p-toluidine, N,N-diethyl p-toluidine, N,N-dimethylsym(m)xylidine, 3,5-di-tert-butyl-aniline, N,N-dimethyl-p-ethyl aminobenzoate), the compounds containing an activated nitrogen and sulfur atom such as the derivatives of thiazole (mercaptobenzothiazole), boron salts (borate) such as tetraphenylborates or butyltriphenylborates, and other salts of tetraalkylammonium tetraorganylborate type.

The system may be considered differently depending upon whether the "intermediate" species or the onium salt is considered as photosensitizer.

Also, another series of examples applicable to the scope of the invention relates to the photosensitization of an onium salt, of triarylsulfonium or diarylhalogenium salt type used, without association, with an electron donor of tertiary amine or borate salt type (but optionally associated with a suitable proton donor). Formulators may then optionally choose to photosensitize through addition of a photosensitive compound enabling triplet-state triplet-state energy transfer chosen from the following list: acetone, 1-indone, acetophenone, 3-trifluoromethyl-acetophenone, xanthone, or by incorporating a photosensitive compound enabling electron transfer with an onium salt chosen from among: anthracene, pyrene, perylene, aromatic ketones such as benzophenone, Michler ketones, xanthenes, thioxanthenes, derivatives of dimethyl aminobenzylidene, phenanthraquinones, eosine, ketocoumarins, acridines, benzofuranes.

For cationic polymerization reaction, the photoinitiating system in addition to the photoinitiator chosen from among the onium salts, also comprises at least one photosensitizer of this photoinitiator. The advantage of this combination is to

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accelerate photopolymerization and to extend the spectral response of the photoinitiation system.

The photosensitization mechanisms of onium salts are complex and the composition of the invention may, as examples, 5 comprise the following combinations (examples have already been given for photosensitization under radical initiation):

- onium salts and aromatic polycycles such as derivatives of anthracene, fluorene, pyrene;
- onium salts and dyes such as xanthene, thioxanthene, 10 merocyanine, acridone, tetrabenzoporphyrine, flavine, acridine;
- onium salts and carbazole derivatives;
- onium salts and metal salts able to achieve electron transfer towards the iodonium salt;
- onium salts and ketones such as thioxanthenes for 15 example, derivatives of benzophenone, ketocoumarins, 1,2-diketones such as camphorquinone, derivatives of anthraquinone;
- onium salts and generators of radicals such as benzoin ether for example, dialkoxyacetophenone or phosphine oxide benzoyl.

20 4- According to a final particularly privileged aspect of this variant of initiation means for the polymerization reaction, the latter are initiation means of photochemical type, whose composition may include at least one photoinitiator, at least one co-initiator, at least one photosensitizer or, more 25 generally, any adequate combination between the different potential components of a photoinitiation system, such as described under 1-, 2- and 3- above, with a view to increasing its efficacy and/or to modify its absorption range of electromagnetic radiation.

30 According to a third variant of the initiation means for the polymerization reaction of the adhesive composition of the invention, the initiation means are of thermal type. This variant can be given more particular consideration for radical polymerization. A great number of thermal radical initiators 35 exist in the literature. Non-limitative examples are: AIBN,

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benzoyl peroxide, tert-butyl hydroperoxide, tert-butyl peracetate, tert-butyl peroxide, dicumyl peroxide and others.

Finally, a last variant of polymerization initiation means is a global variant integrating all possible, compatible combinations of initiation means such as described previously in the first, second and third variants. This choice may prove to be a shrewd choice since it can provide improved crosslinking of the adhesive and improved physicochemical properties. For example, in dental use, a post-polymerization or post-crosslinking agent may be added to a camphorquinone /tertiary arylamine system, the agent possibly being a peroxide such as dibenzoyl peroxide.

To conclude, it will be noted that in the case of a radical polymerization mechanism, the vinyl units forming a donor/acceptor pair presented above are also radical initiation means.

It will be easily understood that formulators may evidently combine several types of bifunctional monomers within one same adhesive composition of the invention. Particular attention must be given to the wavelength ranges used. Preference is given to the combination of bifunctional compounds for which wavelength λ_2 is identical or overlapping, and whose photoinitiation wavelengths λ_1 are fairly different. However, if the photoinitiator used is very efficient and if the concentration of photocleavable units is reasonable, consideration may be given to the overlapping of absorption ranges λ_1 and λ_2 if the kinetics of active centre generation by the photoinitiator are much greater than the kinetics of bifunctional monomer cleavage, which may translate as exposure of the material to lower radiation powers, longer lamp distances etc..

Also, monomers may advantageously be combined which polymerize by different processes, taking care that initiation means for the polymerization reactions are adequated, so as to form interpenetrating networks whose advantages are well known: mechanical synergy, improved resistance over time and increased snatch resistance.

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According to an essential characteristic of the invention, the bifunctional monomers must be present in sufficient quantity in the adhesive composition to obtain loss of integrity and adhesiveness of the hardened composition when it is subjected to uncrosslinking radiation. The minimum quantity is 0.5 weight % of the adhesive composition. The optimum quantity of bifunctional monomers to obtain the desired loss of integrity of the adhesive is related to several parameters, in particular the photoreactivity of the photocleavable units, the structure of the bifunctional monomers, the presence and type of co-monomers or reactive diluents of the adhesive composition. Generally, the quantities are low if the glass transition temperature of the polymerized adhesive is less than -30°C for example, and greater if the adhesive compositions are highly charged and/or crosslinked.

Evidently, the adhesive composition of the invention may, in addition to the bifunctional monomers and initiation means, comprise other constituents in particular:

- co-monomers polymerizable by a chain polymerization mechanism, which may act as reactive diluent, and which may be of same type as the polymerizable units described previously or they may be any polymerizable unit conventionally used in adhesive resins;
- a component carrying at least one thiol function, such as those cited in patents US 4,663,416 and US 4,780,486;
- a polyalkenoic acid such as a copolymer of itaconic and polyacrylic acid, for example,
- various fillers which may be organic and/or inorganic, in particular of silica type (optionally silanized) or of ionomer glass type such as CaF_2 , YF_3 , AlF_3 , more generally suitably formulated fluoroaluminosilicate glasses;
- additives such as those usually used in adhesive compositions and intended to improve some of their physicochemical properties, such as solvents (water and organic), pigments, stabilizers, surfactants, plastifiers, etc..

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The multiple possible combinations enable best adjustment of viscosity or fluidity of the adhesive composition, in relation to needs connected with end use.

5 Also, it will be understood that the photosensitive adhesive composition of the invention is applicable to numerous areas having regard to the multiplicity of possible variants. Special consideration is given to dental use for cementing elements to the surface of teeth and/or to fill dental cavities.

10 In respect of the positioning of bands for orthodontic correction, the enamel surface of the teeth is prepared by cleaning and optional mordant preparation using appropriate products. Then, the adhesive composition of the invention is applied to the prepared area, the bands are placed in position on
15 the adhesive layer which is then hardened by photopolymerization for example.

Once correction has been completed, the bands are removed by subjecting the hardened adhesive to uncrosslinking radiation which disrupts the integrity of the adhesive and makes it
20 possible to separate the bands from the enamel surface of the teeth without causing any mechanical damage to this surface.

The adhesive composition may also be used to ensure temporary closing of a tooth root canal. For this purpose, after conventional root dressing and preparation, the root canal is
25 filled as far as the apex of the tooth with the adhesive of the invention, then a master-cone is inserted inside the root canal of similar length to the root canal. This master-cone is made of material able to convey crosslinking /uncrosslinking radiation on its outer end towards the inside of the tooth and to diffuse the
30 same towards the canal wall so that the root sealing adhesive of the invention can be easily removed without causing any damage to the integrity of the root canal.

Several examples of photosensitive adhesive compositions in the UV/visible ranges especially intended for dental application
35 are given below.

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Evidently, these examples can be transposed to any other industrial sector in which there is a need for temporary adhesiveness, which can be controllably released and without the use of complex or hazardous equipment by operators. Special consideration is given to all systems intended to be subsequently recycled, in which the use of an adhesive of the invention enables very easy separation of various bonded elements.

Attention must be given however to the efficacy of the cleavage generated by uncrosslinking actinic radiation. In this respect it is possible to increase the proportion of bifunctional monomers. It is also possible to contemplate inserting an optic fibre guide inside the bonded joint with an external access point which may be used to transmit actinic radiation for polymerization and then cleavage to the entire bonded joint. The other alternative consists of using the photosensitive adhesive of the invention to bond parts whose material or form are advantageously designed so that they can allow the passing of at least the uncrosslinking wavelength λ_2 , initiation of polymerization possibly being chemical.

Finally, the photosensitive adhesive composition of the invention may evidently comprise bifunctional compounds that are polymerizable and cleavable in wavelength ranges other than those described, and the examples of composition given below are evidently only particular illustrations which do not in any way restrict the areas of application of the photosensitive adhesive composition of the invention.

EXAMPLES OF PHOTOPOLYMERIZABLE FORMULATIONS
OF THE PHOTSENSITIVE ADHESIVE COMPOSITION OF THE INVENTION FOR
USE IN DENTISTRY

In the following examples, the mechanical properties of adhesive compositions were tested whose formulation comprises one or more bifunctional monomers.

The different constituents are dispersed in a minimum volume of ethyl ether. The mixtures are homogenized by ultrasound

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under magnetic stirring and are then concentrated and placed in a vacuum of 4mmHg for one hour.

The formulations are arranged in a Teflon mould whose base is a glass slide to give bars of size (14mm x 4mm x 1 mm) after polymerization. Polymerizations ($\lambda 1$) are conducted using an Efes Lite Mercury-Xenon 50W lamp positioned at a distance of 0.5 cm from the surface of the sample and, unless otherwise indicated, using an interference filter allowing radiation of between 426 and 480nm to pass. The sample is irradiated 150s on each side, unless otherwise specified. Successive irradiations ($\lambda 2$) are performed using the same lamp positioned at 0.2 cm from the sample with an interference filter allowing radiation of between 320 and 480 nm to pass. The sample is irradiated 600s on each side.

The mechanical properties were evaluated with DMA (Dynamic Mechanical Analysis) following a 3 bend-point mode after polymerization at $\lambda 1$ and after degradation at $\lambda 2$.

For all tested compositions, fissuring was observed in the structure of the sample after degradation.

The weight percentages of the constituents marked with an asterisk (*) are given in relation to the total weight of the monomers (all polymerizable organic compounds).

EXAMPLE 1: Cationically polymerizable composition

The composition given below may be used in particular for cementing applications, but can be used for other dentistry operations.

The sample is polymerized by 300s radiation on each side.

| Component | weight % |
|--|----------|
| 3,4-epoxycyclohexylmethyl epoxycyclohexanecarboxylate | 22 |
| Cyclohexene oxide | 4 |
| NTS | 14 |
| Bis-(4-dodecylphenyl)iodinium hexafluoroantimonate* | 1.5 |
| Camphorquinone* | 0.75 |

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| | |
|---|-----|
| Ethyl 4-dimethylaminobenzoate* | 0.4 |
| Cem-bridge type filler (Pierre Rolland dental products) | 60 |

The elastic modulus measured at 25°C after photopolymerization is 2.20 GPa and 0.95 GPa after degradation.

5 EXAMPLE 2: Anionically polymerizable composition

The composition given below may be given particular application for cementing but can be used for other operations in the area of dentistry.

- 10 In this particular case, wavelength λ_1 lies between 400 and 480 nm and polymerization times are 300s on each side.

| Component | weight % |
|---|----------|
| 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate | 4 |
| Bis-(3,4-epoxycyclohexylmethyl)adipate | 20 |
| AT9 | 16 |
| N-methylnifedipine* | 1.5 |
| Cem-bridge type filler (Pierre Rolland dental products) | 60 |

- 15 The elastic modulus measured at 25°C after photopolymerization is 2.40 GPa and 1.15 GPa after degradation.

EXAMPLE 3: Radically polymerizable composition

- 20 The composition given below preferably has clinical applications for cavity filling and cementing, in particular for root canal work, fissures and anchoring.

| Component | weight % |
|----------------------------|----------|
| Bisphenol A dimethacrylate | 9.2 |

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| | |
|---|------|
| Hydroxyethyl methacrylate | 6.2 |
| Butyl methacrylate | 3.6 |
| Triethyleneglycol dimethacrylate | 12.1 |
| PU1AT1 | 30.7 |
| (4-n-decyloxyphenyl)phenyl-iodinium SbF ₆ ⁻ * | 1 |
| Camphorquinone/4-ethyl dimethylaminobenzoate* | 0.5 |
| Benzoyl peroxide* | 0.3 |
| Revolution Formula 2 filler (Kerr) | 38.2 |
| Hydroquinone methyl ether* | 0.2 |

The modulus of elasticity measured at 25°C after photo-polymerization is 2.90 GPa and 0.70 GPa after degradation.

5 EXAMPLE 4: Radically polymerizable composition

The composition given below has preferable clinical application for restorative dental operations using composites.

| Component | weight % |
|---|----------|
| Urethane Dimethylacrylate | 3.4 |
| Butyl Methacrylate | 2.3 |
| Polyethylene glycol dimethacrylate Mn~875 | 2.3 |
| Triethyleneglycol dimethacrylate | 4.5 |
| PH2AT1 | 7.15 |
| AT3 | 3.6 |
| (4-n-decyloxyphenyl)phenyl-iodinium SbF ₆ ⁻ | 1 |
| Camphorquinone/4-ethyl dimethylaminobenzoate * | 0.5 |
| Benzoyl Peroxide * | 0.3 |
| Kappalux M filler (Pierre Rolland dental products) | 76.75 |
| Hydroquinone methyl ether * | 0.2 |

10 The elastic modulus measured at 25°C after photo-polymerization is 8.20 GPa and 1.30 GPa after degradation.

EXAMPLE 5: Radically polymerizable composition

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The composition given below has preferable clinical application for orthodontic cementing, in particular the cementing of metallic and/or ceramic parts to a tooth

| Component | weight % |
|--|----------|
| Urethane dimethacrylate | 5.8 |
| Hydroxyethyl methacrylate | 7.26 |
| Triethyleneglycol dimethacrylate | 5.8 |
| NT4 | 10.20 |
| Irg 819 * | 1 |
| Glycerol Phosphate Dimethacrylate | 1 |
| Cem-bridge filler (Pierre Rolland dental products) | 69.94 |
| Hydroquinone methyl ether* | 0.2 |

5

The elastic modulus measured at 25°C after photopolymerization is 4.65 GPa and 0.80 GPa after degradation.